INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again – beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106

A Xerox Education Company

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

APPLICATION OF PHOTOCHEMICAL PROCESSES IN WASTEWATER TREATMENT

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

HOK-JANG THUNG

Norman, Oklahoma

1972

APPLICATION OF PHOTOCHEMICAL PROCESSES

IN WASTEWATER TREATMENT

APPROVED BY

DISSERTATION COMMITTEE

ACKNOWLEDGEMENT

I wish to take this opportunity to express my deep appreciation to the members of my graduate committee, and in particular to Dr. Leale E. Streebin, chairman of the dissertation committee, whose helpful guidance, understanding and interest were of great encouragement to all my endeavors.

To Dr. John G. Burr, who served as a member of the committee and who contributed to my comprehension of photochemistry, I am indebted.

Acknowledgement is also made to Dr. Larry W. Canter and Professor George W. Reid for having served as members of the dissertation committee.

Gratitude is extended to Gerisue Henry for her editoral and typing assistance.

This investigation was supported by a Predoctoral Research Fellowship from the Federal Water Quality Administration and Environmental Protection Agency, for which the author expresses his sincere appreciation.

The financial aid from the United States Public Health Service, through the Department of Civil Engineering, University of Oklahoma, during the second year of my graduate studies is gratefully acknowledged.

Finally, to my most intimate human environment, my wife and children, I must convey my most affectionate appreciation for their patience and understanding.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

Figure No. Page

Figure No. Page

APPLICATION OF PHOTOCHEMICAL PROCESSES IN WASTEWATER TREATMENT

CHAPTER I

INTRODUCTION

General

The American public's interest has recently been aroused, concerning the topic of environmental quality. It is generally acknowledged that the war on pollution is underway in this country. Pollution has become not only a scientific and technological problem, but a social and political issue as well. It is understandable that the public being aware of the significance of a healthful environment, becomes very impatient and demands that government and industries cope with this complex problem, which resulted from centuries of national carelessness in the use of natural resources. To the scientist and engineer, the public's concern about pollution becomes a challenge and an imperative duty to develop and learn more about the science and technology of existing treatment methods.

Water has remarkable properties and is a good absorbent or solvent for various substances. Another remarkable quality of water is that it can be cleaned when it gets dirty. In fact, it is always possible that water can be reused for various purposes again and again.

Water quality is the crucial factor when quantity and quality are

considered. In spite of an increasing need for water, there is enough water in this country to meet the demand, not only in the years immediately ahead, but on into the future provided we use it properly.

Water quality deterioriation first received attention as a public problem following the outbreak of water borne diseases. Although water pollution is not a new problem, the difference of the contemporary situation is that it is no longer focused solely on health protection but also on aesthetic and recreational aspects. President Johnson in signing the Water Quality Act of 1965 summarized the water pollution problem by stating [47]:

> "The clear fresh waters that were our national heritage, have become dumping grounds for garbage and filth. They poison our fish, they breed disease, they spoil our landscape."

The conventional methods of treatment used for altering the characteristics of liquid waste are based primarily on biological oxidation, biosorption and oxygen transfer processes. These methods which have been studied extensively, developed and modified, can produce a plant effluent of high purity. However, it has become evident that municipal and industrial wastes now include many pollutants that are resistant to or even totally unaffected by the conventional waste treatment process. Such contaminants, refractory or "non-biodegradable" substances, include both organic and inorganic materials. Advanced waste treatment or tertiary treatment processes are required for the removal of these pollutants. Among the tertiary processes being considered are: adsorption, electrodialysis, reverse osmosis, corona discharge oxygenation, distillation, ion exchange, etc. There is no question about potentiality and technical feasibility, but as is often the case economical consideration is a

crucial factor.

For the removal of organic refractory materials, adsorption, coagulation and chemical oxidation are considered to be the most promising types of operation. Adsorption has the advantage of being applicable for the removal of a wide variety of organic compounds. The forces of adsorption are generalized and primarily physical; consequently, adsorption is not as nearly limited to the same extent by the chemical structure of the organic contaminants as are many other methods. Adsorption on activated carbon has long been recognized as one of the basic unit operations for the purification of solutions. Activated carbon treatment of liquids is a relatively simple operation requiring a minimal physical plant and no elaborate specialized equipment. Although the economic and technical feasibility of granular activated carbon treatment has been established, the application has been primarily limited to the polishing of the secondary effluent.

Powdered activated carbon adsorbs soluble organic wastewater just as granular carbon does. Because of the much smaller average particle size, the adsorption per unit weight of adsorbent can be expected to be more efficient; however, the small particle size results in a high pressure drop for the fixed bed operation. A suitable and efficient procedure for reactivation of the exhausted carbon is absolutely needed to make powdered carbon use become economically feasible.

Interest in chemical coagulation as a possible means for attaining a higher degree of wastewater purification is quite understandable. This process for many years has been one of the most widely used and most versatile water treatment methods. Research work in coagulation processes

is throwing new light on basic principles, and coagulation is becoming more of a science than an art.

The use of organic coagulants and coagulation aids is becoming common. Studies have been reported on the use of anionic, cationic, nonionic coagulant aids, and the evaluation of natural and synthetic polyelectrolytes. The main problem with the use of coagulation, in the further treatment of sewage, is its relative ineffectiveness in the removal of soluble impurities.

Chemical oxidation has the potential of removing organics commonly used to treat wastewater, which are not oxidizable by biological processes. The oxidation products will be primarily carbon dioxide, water, nitrogen oxide and oxides of other elements. Oxidation methods that might be employed include the use of ozone, hydrogen peroxide, the hydroxyl free radical, oxidation with molecular oxygen, catalytic oxidation with molecular oxygen, electrochemical treatment, etc. As organic materials have different reactivities toward oxygen, this oxidation process is very dependent on the selectivity of the reactions. Unless catalyst or reaction conditions can be found to make the oxidant less discriminating, it is unlikely that the mentioned oxidizing agents can serve as reagents for general solutions.

Problem

The aim of advanced waste treatment is focused on the removal of the remaining contaminants that are resistant to conventional treatment methods. These contaminants are referred to as refractory or non-biodegradable materials. The term non-biodegradable, which is commonly understood by sanitary engineers, is actually a misnomer. It is true that some compounds are totally resistant to biological decomposition under all

circumstances; however, in wastewater treatment the pollutants which fail to be removed under the process conditions are often classified as non-biodegradable. The infallibility principle has been clearly and briefly summarized by Gale [1]:

> "It is probably not unscientific to suggest that somewhere or other some organisms exist which can, under suitable conditions, oxidize any substance which is theoretically capable of being oxidized."

Without question, many compounds persist and are not degraded under certain environmental conditions. This may result from factors which entirely preclude growth or metabolism. On the other hand, it is a fact that there are indeed recalcitrant molecules, substances that are totally resistant to biological decomposition under all circumstances. This resistance is not due to the absence of favorable conditions for the biochemical reaction to occur, but is usually inherent to the chemical structure of the substance itself.

In general, the rate of any chemical reaction is dependent on the reactants and their concentrations. In waste treatment systems, the reactants are the specific waste components and the enzyme systems are provided by the organisms. Even if all the necessary enzyme systems are present, some compounds are removed at a faster rate than others.

The recalcitrance of some molecules to biological degradation can be attributed to:

1. Their structure. Because of the size of high molecular weight compounds, direct penetration of the cell membrane is not possible unless the large molecules are broken into smaller fragments by hydrolytic enzymes.
2. Repression and inhibition effects.

High molecular weight organic materials tend to resist biodegradation; however, there are exceptions and the contrary is not necessarily true. Oxalic acid and some low molecular weight amines are non-biodegradable. Nevertheless, long chain fatty acids can be metabolized quite readily. Despite the absence of a direct relationship between molecular size and biodegradability, fragmentation of large molecules will generally make the penetration through the membrane easier, and enable the organism to metabolize the compounds.

In biochemical systems, it is commonly known that hydrolytic enzymes are responsible for the degradation process [18]. For large complex polymeric substances several different enzymes are necessary to accomplish degradation, and more than one kind of organism may be needed to supply these enzymes. Unfortunately, necessary hydrolytic enzymes or organisms are not always available in a wastewater treatment system. In those systems non-biological degradation of the refractory materials may contribute significantly to the control of environmental contamination. Photolysis or radiolysis, coupled with oxidation, is one of the non-biological degradation processes that has some practicalities in wastewater treatment.

Objective

The purpose of this study is to investigate the practicality and feasibility of photodegradation, photooxidation and photosensitized oxidation in the fragmentation of refractory organic materials that are likely to be found in plant effluents.

Photodegradation, photooxidation and photosensitized oxidation have been studied extensively by chemists during the past two decades; however; application in wastewater treatment is just beginning. Because of the

complexity of the reactions involved, it is deemed justifiable to focus on a simplified system, but with anticipation that the data obtained from these investigations can be used for a better understanding of the process.

The scope of this research work will be limited to the study of photodegradation and photooxidation, direct and indirect, of some organics having particular molecular structures known to be slowly biodegradable. Several reaction parameters are to be investigated and tests on the susceptibility of reaction products to biodegradation will be conducted. No attempt will be made to acquire the knowledge of the reaction mechanisms of the process, as this is beyond the scope of the work.

Justification

The theory of photooxidation and photosensitized oxidation is well understood and established. It is then the duty of scientists and engineers to explore the potentiality and practicality of the existing theories to cope with the acute pollution problem. The conventional biological waste treatment process has proven inadequate in removing certain recalcitrant materials, and physical-chemical processes are generally too costly. A combination of biological, physical and chemical processes might be one solution, another could be the use of light sensitized reactions. Based on this rationale the study of photochemical reactions in wastewater treatment is justifiable.

CHAPTER II

LITERATURE REVIEW

Basic Theories of Photochemistry

The Law of Photochemistry

In photochemical reactions the activation energy is provided by the absorption of light photons by the system. Grotthurs (1817) and Draper (1943) formulated the first law of photochemistry as follows: Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule [8].

It is known that there must be some overlap between wavelengths of light entering a reaction cell and those absorbed by the desired compound, or activator, if a light reaction is to occur. However, for definitive and quantitative studies, the law must be applied to all aspects of a given photochemical system.

At the beginning of the century, Stark (1908-1912) and Einstein (1912-1913) deduced the second law. Their original law stated that each molecule taking part in chemical reaction caused by light absorbs one quantum [8]. Subsequently, Stark and Bodenstein (1913) pointed out that the second law as stated could only be applied to the primary process since secondary thermal chain reactions could follow the primary process leading to overall quantum yields greater than one. Hence, the second

law was restated; the absorption of light by molecules is a one quantum process, so that the sum of the primary process quantum yield, ϕ, must be unity, that is $\Sigma\phi_i = 1$, where ϕ_i is the quantum yield of the ith primary process. The quantum yield, ϕ, is defined as:

$$\phi = \frac{\text{number of reacting or formed molecules}}{\text{number of quanta absorbed per unit volume and time}}$$

The primary process involved may include dissociation, isomerization, fluorescence, phosphorescence, radiationless transition and all reaction paths which result in the destruction and deactivation of the excited state molecules.

The absorption of monochromatic beams of light by a homogeneous absorbing system is formulated by combining Beer's and Lambert's Law. The form commonly employed in photochemistry is:

$$\frac{I}{I_o} = 10^{-\varepsilon c\, l} \qquad (1)$$

where:

I_o = light energy of incident light per unit time.

I = light energy per unit time transmitted through column of material, 1 cm. in length.

c = concentration, mole/liter.

ε = molar extinction coefficient, liter/mole-cm.

When more than one absorbing compound is present in a homogeneous mixture, the Beer-Lambert Law assumes the form:

$$\frac{I}{I_o} = 10^{-(\Sigma\varepsilon_i c_i)\, l} \qquad (2)$$

where:

c_i = concentration of ith compound.

ε_i = extinction coefficient of the ith compound at a particular wavelength.

A quantum of light of frequency, ν, has an energy represented by:

$$E = h\nu = hc/\lambda \qquad (3)$$

and

h = Planck's constant, 6.625×10^{-27} erg-sec/quantum.

$c = 2.9979 \times 10^{10}$ cm/sec.

λ = wavelength.

ν = frequency.

A photochemist usually employs terms of Kilo-calories of energy and moles of material. The relation between the wavelength or frequency of light and the energy associated with 1 mole of photons, which is defined as an einstein, becomes:

$$E = \frac{Nhc}{\lambda} = \frac{2.859 \times 10}{\lambda(\text{in A})} = \text{Kcal/einstein} \qquad (4)$$

where:

N = Avogadro number, 6.0225×10^{23}

The lowest bond energy in organic compounds is in the range of about 40 Kcal/mole; from this, one can calculate that to be effective in photodissociation, the wavelength must be no longer than 7000 $\mathring{A}$.

Interaction of Light with Molecules

The interaction of photons with molecules and the physical and chemical processes which follow absorption of light are of great interest to the photochemist. The overall interactions can be differentiated into primary physical and primary photochemical processes. The first includes: thermal quenching, fluorescence, phosphorescence, internal conversion and intersystem crossing. The photochemical process is primarily the formation of molecules in the excited state and the production of free radicals. These

lead to further chemical reactions, such as polymerization, oxidation, isomerization, etc.

The primary physical processes can be best described by the Jablonsky Diagram (Figure 1). The definitions for these processes are:

1. Internal conversion --non-radiative transition between states of like multiplicity.
2. Fluorescence --radiative transition between states of like multiplicity.
3. Phosphorescence --radiative transition between states of different multiplicity.
4. Intersystem Crossing --non-radiative conversion between states of different multiplicity.
5. Quenching --deactivation of an excited species by other components of the system.
6. Singlet and Triplet States --multiplicity of a species given by 2S+1, where S is the total electron spin. If S = 0, i.e. the electrons are paired, the spins cancel and the species is singlet. If two electrons have parallel spins, then s = 1 and the species is triplet.

The primary photochemical processes which occur due to excitation of molecules are summarized in Table I [8].

The quantitative theoretical prediction of the nature and efficiency of the possible primary processes which occur as the intermediate result of light absorption is not possible even for simple molecules. However, one can find that systematic patterns and correlations exist between chemical structures and photochemical reaction modes. Using these patterns,

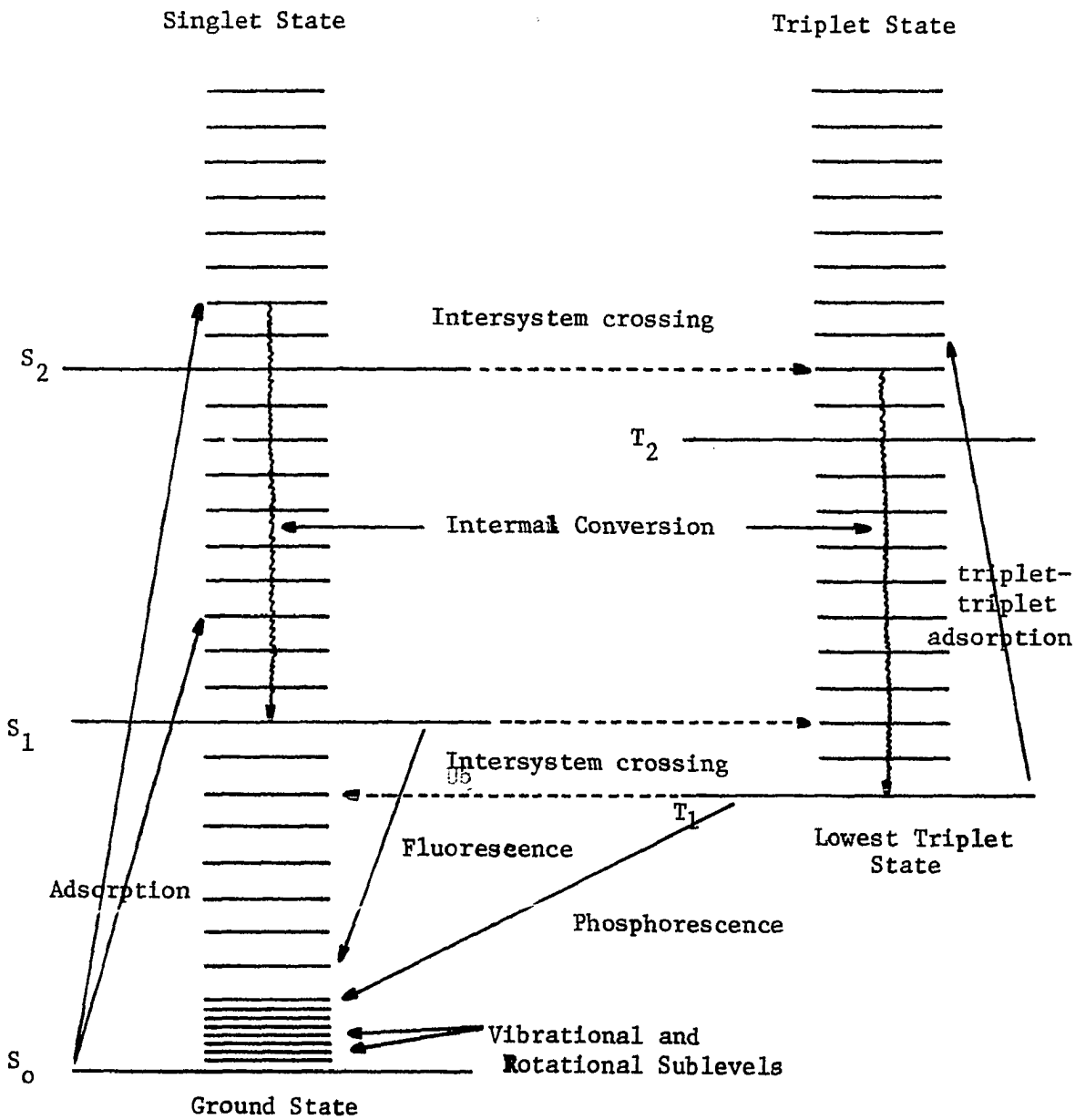


Figure 1. Primary Physical Processes (According to Jablonski)

TABLE I

PRIMARY PHOTOCHEMICAL PROCESS*

$ABC(S_1)$	$\rightarrow AB\cdot + C\cdot$	Dissociation into radicals
	$\rightarrow E + F$	Intramolecular decomposition into molecules
	$\rightarrow ACB$	Intramolecular rearrangement
	$\rightarrow ABC'(S_1)$ or $ABC'(T_1)$	Photoisomerization
	$\rightarrow ABC'(S_o)$	
or		
$ABC(T_1)$	$\xrightarrow{RH} (ABCH)\cdot + R\cdot$	Hydrogen atom abstraction
	$\xrightarrow{ABC} (ABC)_2$	Photodimerization (photo-addition)
	$\xrightarrow{D} ABC + \text{product}$	Photosensitized reaction
	$\rightarrow ABC^+ + e^-$	Photoionization
	$\xrightarrow{D} ABC^+(\text{or } -) + D^-(\text{or } +)$	"External" electron transfer
	$\rightarrow AB^+ + C^-$	"Internal" electron transfer

*(After Calvert and Pitt.)

one can make a reasonable prediction as to the nature and extent of the primary processes expected in related compounds that have not been studied.

Notation for Electronic States of Diatomic Molecules

The notations for the state of diatomic molecules that will be used in the following chapters are Σ and Δ. Analogous to the electronic configuration of atoms, the electronic states of a diatomic molecule are classified in terms of several molecular quantum numbers. The first of these, Λ, is the component of the total electronic orbital angular momentum, L, along the internuclear axis. Values of Λ: 0,1,2,3; are classified as Σ, π, Δ, and Φ states. The molecular quantum number, S, is the sum of vectors of the individual electron spin moments in units of $h/2\pi$, analogous to atoms. When only positive values and zero represent S, the multiplicity state is 2S+1, just as with atoms.

In addition to these quantum numbers, certain other properties of the MO, Molecular Orbital, must be specified to completely define its energy. If wave function, ψ, changes sign when the coordinates of all the electrons are replaced by their negative values, the state is ungerade, "u"; otherwise, the state is gerade, "g". These symbols are indicated as subscripts to Λ.

Symbols + and -, written as subscripts to Λ, refer to two types of sign states, Σ^+ and Σ^-. The state is positive if ψ is unaltered by reflection about a plane through the two nuclei, and negative if ψ changes.

Using these notations, the ground state and two singlet states of oxygen are represented by:

$$^3\Sigma_g^-,\ ^1\Sigma_g^+ \text{ and } ^1\Delta_g$$

Selection Rules

The selection rules [8,19,36,47] that will be encountered have a wave mechanical background with a radiative electronic transition that may be classified as "allowed", high probability, or "forbidden", low probability. In actual practice with polyatomic molecules the selection rules often break down sufficiently to permit reasonably strong absorption processes to occur. One "forbidden" transition of great importance in this discussion of photooxidation is spin forbidden. For example, radiative transition involving a change of spin or multiplicity is strongly forbidden. Thus, single triplet transition or intersystem crossing is forbidden; however, real states are not purely singlet or triplet, and the crossing phenomena occurs with lower probability than ordinary internal conversion.

Basic Kinetics of Photochemical Reaction [5,8,34]

In photochemical kinetics, as in thermal kinetics, there can be no general formulation of all changes that can take place even in simple systems. After excitation, a radical or molecule may:

1. Lose its energy by spontaneous emission of a quantum, $h\nu$;
2. Decompose chemically;
3. Or be deprived of its energy by collisions with molecules of its own kind or of another kind.

The scheme will then be:

$$A + h\nu \longrightarrow A^*$$

$$A^* \longrightarrow A + h\nu$$

k_o = excitation by absorption of radiation.

k_1 = fluorescence or spontaneous emission or radiation.

$A^* \longrightarrow P$	k_2 = spontaneous chemical conversion to product P.
$A^* + A \longrightarrow 2A$	k_3 = deactivation by collision of its own kind.
$A^* + B \longrightarrow A + B$	k_4 = deactivation by collision with molecules of B.

Denoting "a" as the concentration of excited radicals or molecules, and "n" as the concentration of other species --the rate of production, then A^* becomes:

$$\frac{da}{dt} = k_o n_A - k_1 a - k_3 a - k_2 a n_A - k_4 a n_B \tag{1}$$

The stationary condition of the active or excited species is found when $da/dt = 0$, hence:

$$a = \frac{k_o n_A}{k_1 + k_3 + k_2 n_A + k_4 n_B} \tag{2}$$

The rate of chemical change is $k_3 a$. It is concluded that the rate of increase in the concentration of product molecule is:

$$\frac{dn_p}{dt} = \frac{k_o k_3 n_A}{k_1 + k_3 + k_2 n_A + k_4 n_B} \tag{3}$$

If the activated molecule is more likely to undergo chemical change than any of the other possible changs, or if k_3 is the dominant term, then:

$$\frac{dn_p}{dt} = k_o n_A \tag{4}$$

It is also known that $k_o = k_{ij} n_v$, where k_{ij} is the first of the Einstein three coefficients and n_v is the concentration of photons in the irradiating beam.

Introducing the absorption coefficient, α, which is defined as:

$$\alpha = k_{ij}/c = k_o/n_v c \tag{5}$$

and the light intensity, $I = cn_v h\nu$, where c is the velocity of light, becomes:

$$k_o = n_v c\alpha = \frac{n_v \alpha I}{n_v h\nu} = \frac{\alpha I}{h\nu} \tag{6}$$

or

$$\frac{dn_p}{dt} = \alpha\left(\frac{I}{h\nu}\right) n_A \tag{7}$$

which is the simplest law of photochemical kinetics. That is, the rate of formation of product P follows the first order kinetics with respect to A.

Sensitization [17,26,39]

From earlier discussion it has been noted that excited molecules can be deactivated by energy transfer in the form of vibrational energy to the surrounding solvent, or to molecules of the same species by a process that involves collision. This released energy can be utilized to excite another species electronically, provided certain conditions are satisfied. In order for energy transfer to occur, the following conditions must prevail [19]:

1. The donor excited state must be sufficiently long lived to transfer its energy to an acceptor before various non-radiative or radiative decay reactions occur.
2. The excited energy of the acceptor should not exceed that of the donor; otherwise, the process would be endothermic and therefore, impossible.
3. In accordance with the selection rules, the total spin must be conserved.

When these conditions are satisfied, very efficient energy transfer can take place. This energy transfer, which is followed by emission or reaction of the acceptor, is called sensitization. Properly speaking, the donor or sensitizer will be transformed to its original state and resume its function as a photon absorber. However, in the absence of an acceptor, or if the acceptor concentration is relatively low as compared to that of the donor, the sensitizer will undergo a chemical or physical reaction, which will result in the ineffectiveness of its photosensitization.

Photooxidation and Photosensitized Oxidation

Introduction

Photochemical reactions of organic substrates with molecular oxygen have been extensively studied with respect to their preparative and mechanistic aspects [3,14,15,17,26,28,42,43], i.e. the studies were emphasized on the production of oxygenated compound(s) and the reaction mechanisms involved. Photooxygenation can be classified into two major types, namely:

1. Type I Oxygenation in which free radicals and electronically excited species are involved;
2. Type II Oxygenation in which only electronically excited species occur as intermediates, and the reaction can be either direct or indirect, photosensitized.

Type I oxygenation is also characterized by the occurrence of chain reactions and the following reaction scheme can be assumed:

$RH + h\nu \longrightarrow (RH)^*$ absorption

$(RH)^* + RH \longrightarrow (RH)_2$ dimerization

$(RH)^* \longrightarrow RH + h\nu$ flourescence

$(RH)^* \longrightarrow R\cdot + H\cdot$ free radical formation

After the free radicals are formed, the chain reactions will follow the common pattern, i.e. initiation, propagation and termination.

Initiation: Free radicals source $\longrightarrow R\cdot$

Propagation: $R\cdot + O_2 \longrightarrow RO_2\cdot$

Termination: $RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$

$2R\cdot \longrightarrow R\text{-}R$

$R\cdot + RO_2 \longrightarrow ROOR$

$2RO_2\cdot \longrightarrow ROOR + O_2$

etc.

Depending on the system conditions and the chemical properties of the products, R-R, ROOR, etc., these compounds can undergo decomposition resulting in smaller fragments or stable end products.

Type II oxygenation can be summarized by the reaction scheme introduced by Gollnick [14,17]:

Direct	Indirect
$A + h\nu \longrightarrow A^*$	$S + h\nu \longrightarrow S^*$
I. Acceptor-Activation Mechanism	
$A^* + O_2 \longrightarrow AO_2$	$S^* + A \longrightarrow S + A^*$
Direct Combination	Energy Transfer
	$A^* + O_2 \longrightarrow AO_2$

Direct	Indirect
$A^* + A \longrightarrow (AA)^*$	$S^* + A \longrightarrow (SA)^*$
Complex Formation	Complex Formation
$(AA)^* + O_2 \longrightarrow A + AO_2$	$(SA)^* + O_2 \longrightarrow S + AO_2$

II. Oxygen-Activation Mechanism

$A^* + O_2 \longrightarrow A + O_2^*$	$S^* + O_2 \longrightarrow S + O_2^*$
Energy Transfer	Energy Transfer
$O_2^* + A \longrightarrow AO_2$	$O_2^* + A \longrightarrow AO_2$
$A^* + O_2 \longrightarrow (AO_2)^*$	$S^* + O_2 \longrightarrow (SO_2)^*$
Complex Formation	Complex Formation
$(AO_2)^* + A \longrightarrow A + AO_2$	$(SO_2)^* + A \longrightarrow A + AO_2$

where:

A	= substrate
A^*	= singlet or triplet excited A
$(AA)^*$, $(AO_2)^*$	= electronically excited complexes
S	= sensitizer
S^*	= singlet or triplet excited S
$(SA)^*$, $(SO_2)^*$	= electronically excited complexes

In many cases, the substrate A will have an absorption peak at short wavelength range. From the above schemes, it can be concluded that Type II direct and Type I Photooxygenation can only be efficient under the exposure of UV and far UV spectrum.

Some of the substrates, organic compounds, that have an absorption peak at the UV range are: organic acids and esters, below 2500 Å; alcohols and ethers, below 2000 Å; aliphatic amines, below 2500 Å; and phenols,

2380 Å and 2780 Å.

It is generally true that operating at a near or far UV region is costly and less efficient, primarily because of the light source and the absorption of the effective spectrum by the material of the immersion well and cooling system. On the other hand, many sensitizers for photooxidation are colored materials, dyes or pigments, and hence, light of the visible spectrum can be applied to the process [8,19,47].

Reaction Processes in Photosensitized Reactions

Bourdon and Schnuriger [6] introduced the following scheme as described in Figure 2 to illustrate the overall reactions. This diagram shows the deactivation process of the sensitizer molecule from its triplet state to ground state. Competition between these reactions will determine the route and efficiency of the reaction.

Bourdon and Schnuriger pointed out that among these processes two reactions can lead to a chemical transformation. These reactions of a triplet sensitizer with oxygen and a reducing compound are shown below:

$$^3D_1 + O_2 \longrightarrow \begin{pmatrix} (D\text{--}O_2) \\ {}^1D_o + (O_2)^* \end{pmatrix} \xrightarrow{RH} {}^1D_o + \text{product} \qquad (1)$$

$$^3D_1 + RH \longrightarrow \begin{pmatrix} D^- + RH^+ \\ R\cdot + DH\cdot \end{pmatrix} \xrightarrow{O_2} {}^1D_o + \text{product} \qquad (2)$$

The first equation result illustrates oxygen transfer and the second illustrates the transfer in electron or hydrogen abstraction. In both cases the sensitizer is regenerated but the oxidation products are not necessarily the same. An inherent competition between reaction (1)

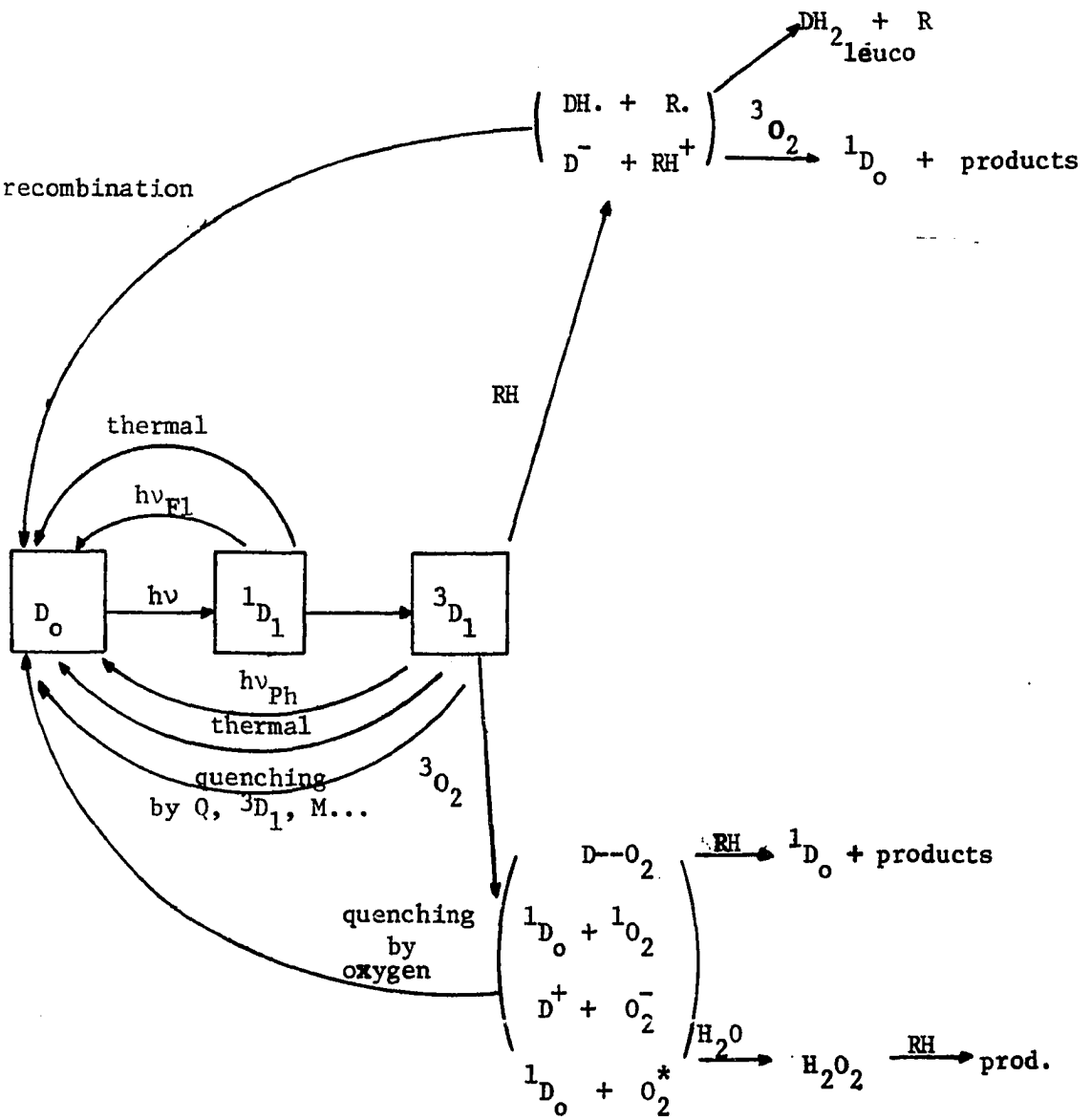


Figure 2. Major Reaction Processes in Photosensitized Reaction (After Bourdon and Schnuriger).

and (2) exists. Depending upon the nature of the sensitizer, the matrix and the experimental conditions, the first of the second will be favored. $(D{-}{-}O_2)$ is the metastable peroxide postulated by Schenck as being the necessary intermediate in photosensitized oxidation.

When the photosensitized reactions take place in a solid matrix or involve absorbed compounds, the relative importance of reaction (1) and (2) can be modified. The conditions imposed by the medium can favor the reaction of the triplet sensitizer, $^3D_1$, with oxygen or the reducing substrate. For example, when the sensitizer molecule is separated from the reducing molecule, it can be predicted that the only possible reaction is photosensitized oxidation by the intermediate of an activated oxygen molecule, i.e. reaction (1). But, if oxygen is of low concentration or if the sensitizer is in close interaction with the reducing substrate, the direct reaction between them is likely to occur via reaction (2). Photosensitized oxidation of an organic compound in which the sensitizer and the oxidizable compound are separated will be reviewed later in this chapter.

Nature of Sensitizers

Figure 2 shows that the occurrence of photosensitized oxidation is highly dependent on the existence of $^3D_1$, or the triplet excited state of the sensitizer. The fact that sensitization involving the triplet state is more favorable than that involving the singlet state is obvious from the longer life-time of the former; i.e. the intersystem crossing, $^3D_1 \longrightarrow {}^1D_o$, is actually spin forbidden.

The sensitizer of photochemical reactions can be grouped into three different classes [6] according to their main characteristics. This

classification which follows is somewhat crude and limited to dye sensitizers.

Class I includes dyes which have a higher reactivity for oxygen than for a reducing agent. Their lowest excited state is probably a triplet, $T_1(\pi, \pi^*)$. They are flourescent, photoreducible and sensitize various photoreactions by their triplet state. They belong to the xanthene type dyes: acridine, thiazine, some porphyrines and riboflavin.

Class II includes dyes which react readily with hydrogen donors by abstracting a hydrogen atom. Their lowest excited state is triplet, $T_1(n, \pi^*)$. Vat dyes and derivatives of anthraquinone belong to this Class.

Class III dyes are closely related structurally to Class II, but have moderate reactivity to oxygen. Their triplet state is considered to be $T_1(\pi, \pi^*)$, a fact that indicates they may also be related to Class I.

Due to the importance of Class I sensitizers in this research work, the review will be confined to this type of sensitizing dye. As mentioned previously in this chapter, one of the conditions favoring the sensitized reaction is that the energy of the donor, excited triplet state of the sensitizer, should be higher than that of the acceptor, oxygen. Chambers and Kearns [10] have investigated the triplet states of some common photosensitizing dyes. Singlet and triplet energy levels of organic dye monomers are listed in Table II.

In most sensitization reactions, rather concentrated dye solutions are used and consequently dimers are the predominant sensitizing species. Chambers and Kearns found that to calculate the energy of the dimer triplet states, 1.2 ± 0.3 Kcal should be substracted from the monomer energies.

TABLE II

SINGLET AND TRIPLET ENERGY LEVELS OF ORGANIC DYE MONOMERS

Dye	$T \longrightarrow S_o$ (Kcal)	$S_o \longrightarrow S$ (Kcal)
Acridines		
Acridine Orange	49.2	56
Acriflavin	51.1	59
Isoalloxazones		
Riboflavin	50	57.8
Xanthenes		
Fluorescein	47.2	55
Eosin B	45.5	52
Eosin Y	45.5	52.5
Rhodamine B	43	49.3

Oxygen quenches the sensitizer phosphorescence and according to Kautsky, a pioneer in photosensitized oxidation studies, the quenching process comes from an energy transfer from the excited dye to oxygen raising the oxygen molecule to its excited singlet states, $^1\Sigma_g^+$ and $^1\Delta_g$. These electronically excited singlet states of oxygen are located 37.5 Kcal and 22.5 Kcal above the triplet ground state. It is then obvious that the energy transfer from excited triplet sensitizer, with an energy level ranging from 43 to 51 Kcal, to ground state oxygen forming two singlet states is thermodynamically possible. The nature of singlet oxygen will be discussed later in more detail.

Some inorganic pigments such as ZnO, ZnS and TiO_2, are known to possess sensitizing properties. Egerton [6] conducted experiments on the tendering of cellulose fibres by some sensitizers. These results are summarized in Table III.

TABLE III

DEGRADATION OF UNDYED COTTON EXPOSED 50 MINUTES IN SUNLIGHT*

	% loss in tensile strength
No film of sensitizer	10-13
TiO_2	30
ZnO	66
ZnS	67
Caledon Yellow 5 G	47
Eosin	76
Acriflavin	100

*placed over films of sensitizer in air at 100% relative humidity.

Egorton's experiment showed the occurrence of sensitized oxidation "at a distance", or where the oxidizable compound and sensitizer are held at a distance from each other. These phenomena had been studied earlier by Kautsky. He suggested that the oxidizing species were singlet oxygen that had met objections as to the nature of the oxidizing entity, and could just as well have been: O_2^-, HO_2, vibrationally excited O_2 or hydrogen peroxide.

Oxidation Species

Since the pioneering work of Kautsky, there has been disagreement on the oxidation entities in the photosensitized oxidation. It has been proposed that the oxidation species could be O_2^-, HO_2, excited O_2 and H_2O_2. Several hypotheses have been made concerning the nature of the oxidizing agent and according to Egorton it could be:

1. In the absence of water, an activated form of oxygen, such as $^1O_2$, O_2^- or O_2^*, vibrationally excited, which is able to perform oxidation only at a short distance or under low oxygen pressure.
2. In the presence of water, hydrogen peroxide, which is able to perform oxidation at long distances.

Hydrogen Peroxide

Water absorbs radiation to a significant extent at wavelengths below 2000 Å, and the spectrum of the vapor is continuous to a first peak at 1650 Å [3]. In this wavelength region there is sufficient energy for primary reactions.

$$H_2O + h\nu \longrightarrow H_2 + O \qquad -117 \text{ Kcal/mole}$$

$$H_2O + h\nu \longrightarrow H + OH \qquad -118 \text{ Kcal/mole}$$

It is of interest to mention that while radiolysis of water produces hydrated electrons as the dominant species, in photolysis of water, the yield in hydrated electrons is less than 10% of the hydrogen atom yield, and only one sixth of the hydrogen atoms produced in photolysis give hydrogen gas as compared to 50% in radiolysis.

There is some uncertainty about the formation of hydrogen peroxide in the photolysis of aerated water unless a sensitizing material is present. A considerable number of studies on photosensitized decomposition of water have been reported, of which are of the more interesting is the decomposition sensitized by zinc-oxide [11,31]. In the absence of molecular oxygen no reaction occurs, but hydrogen peroxide is formed when oxygen is present and one mole of oxygen is consumed per mole of hydrogen peroxide formed. The reaction is suggested as follows:

1. Electron transfer to a water molecule, a primary process.

$$ZnO \cdot H_2O + h\nu \longrightarrow ZnO^{+}H_2O^{-}$$

2. Immediate dissociation of H_2O^{-}.

$$ZnO^{+}H_2O^{-} \longrightarrow ZnO^{+}OH^{-} + H$$

3. Formation of HO_2.

$$H + O_2 \longrightarrow HO_2$$

4. Recombination reaction.

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

Markham and Laidler [31] conclude that the possibility of zinc

peroxide formation was excluded due to the fact that the peroxide was found entirely in solution. The quantum yield for this photosensitized oxidation was 0.25 in the absence of organic materials, and 0.5 when a small amount of phenol was added to the system. They also found that the activation energy was 3 to 4 Kcal.

Semi-Reduced Oxygen, O_2^-

The reaction of oxygen with dyes in their triplet state --xanthene dyes in particular, results in the production of a semi-oxidized radical and semi-reduced oxygen molecule. The reaction scheme proposed by Weis and Uri [6] is as follows:

$$^3D + O_2 \longrightarrow D^+ + O_2^-$$

$$O_2^- + H^+ \longrightarrow HO_2$$

Following Weis's ideas, Egorton tried to confirm that "activated" oxygen was the semi-reduced oxygen molecules, O_2^-. This postulation was based on the similarity of the photosensitizing properties of eosin, acriflavin, the white pigments of ZnO, ZnS and TiO_2, and various vat dyes. Irradiation of these sensitizing materials by light in the presence of water and oxygen results in the formation of hydrogen peroxide is explained by the following reactions:

$$Sens^* + O_2 \longrightarrow Sens^+ + O_2^-$$

$$O_2^- + H^+ \longrightarrow HO_2$$

$$2HO_2 \longrightarrow H_2O_2 + O_2$$

The formation of hydrogen peroxide requires O_2^- as an intermediate. In the case of ZnO, Egorton pointed out that electrons excited by light are raised to the conduction band of ZnO and are then trapped at the surface by

physically absorbed oxygen.

$$O_2 + \text{electron} \longrightarrow O_2^-$$

Physically Absorbed — Chemically Absorbed

Then O_2^- reacts with H^+ and yields hydrogen peroxide.

The formation of hydrogen peroxide can be better explained by the participation of the O_2^- ion than through the intermediation of excited singlet oxygen, $^1O_2$, or vibrationally excited oxygen, O_2^*, for which little information is presently available concerning the possibility of such a reaction. These views are strongly supported by flash photolysis experiments performed by Lindqvist on aqueous solutions of flourescein in the presence of oxygen [20]. In these solutions, oxygen acts as an efficient quencher;

$$^3D + O_2 \longrightarrow {}^1D + O_2$$

or chemical quencher.

$$^3D + O_2 \longrightarrow D^+ + O_2^- \text{ (or } H_2O_2)$$

The production of semi-oxidized dye by these reactions is appreciable and it seems quite reasonable to conclude that O_2^- and D^+ can play the roles of intermediates in photosensitized oxidation.

Vibrationally Excited Oxygen, O_2^*

Rosenberg, et. al. [6], on the basis of experiments similar to the ones of Kautsky, have suggested that the activated form of oxygen may be vibrationally excited molecular oxygen. They studied the phosphorescence of acriflavin absorbed on a silica gel particle and concluded that the reactions involved were:

1. Excitation of oxygen to vibrational state, represented: by O_2^*,

$$^3D + O_2 \longrightarrow {}^1D + O_2^*$$

2. And a reaction of O_2^* with another dye molecule in its triplet state.

$$O_2^* + {}^3D \longrightarrow \text{Product} + h\nu$$

Excited Singlet Molecular Oxygen, $^1\Sigma_g^+$ and $^1\Delta_g$

Originally, Kautsky made the postulation that the oxidizing entity was oxygen in its meta-stable singlet excited state, $^1\Sigma_g^+$, characterized by an energy of 37.3 Kcal above the ground state --λ = 7620 Å. He later pointed out that another excited state oxygen of lower energy could be responsible for photosensitized reactions at wavelengths greater than 7600 Å. Singlet molecular oxygen, $^1\Delta_g$, having an energy of 22 Kcal above ground state will allow the photosensitized reaction to occur with light up to 12,610 Å. The potential energy curves of oxygen are illustrated in Figure 3.

Despite the pioneering works of Kautsky more than thirty years ago, it was not until recently that photochemists came to the conclusion that singlet molecular oxygen plays an important role in a surprisingly diverse number of areas, i.e. dye-sensitized photooxidation, chemiluminescence reaction, upper atmosphere chemistry, degradation of materials, etc. [17].

Singlet molecular oxygen can be produced by chemical or physical methods. A summary of those methods now in use is given below:

1. Chemical Method

   a. reaction of hydrogen peroxide with hypochlorite or

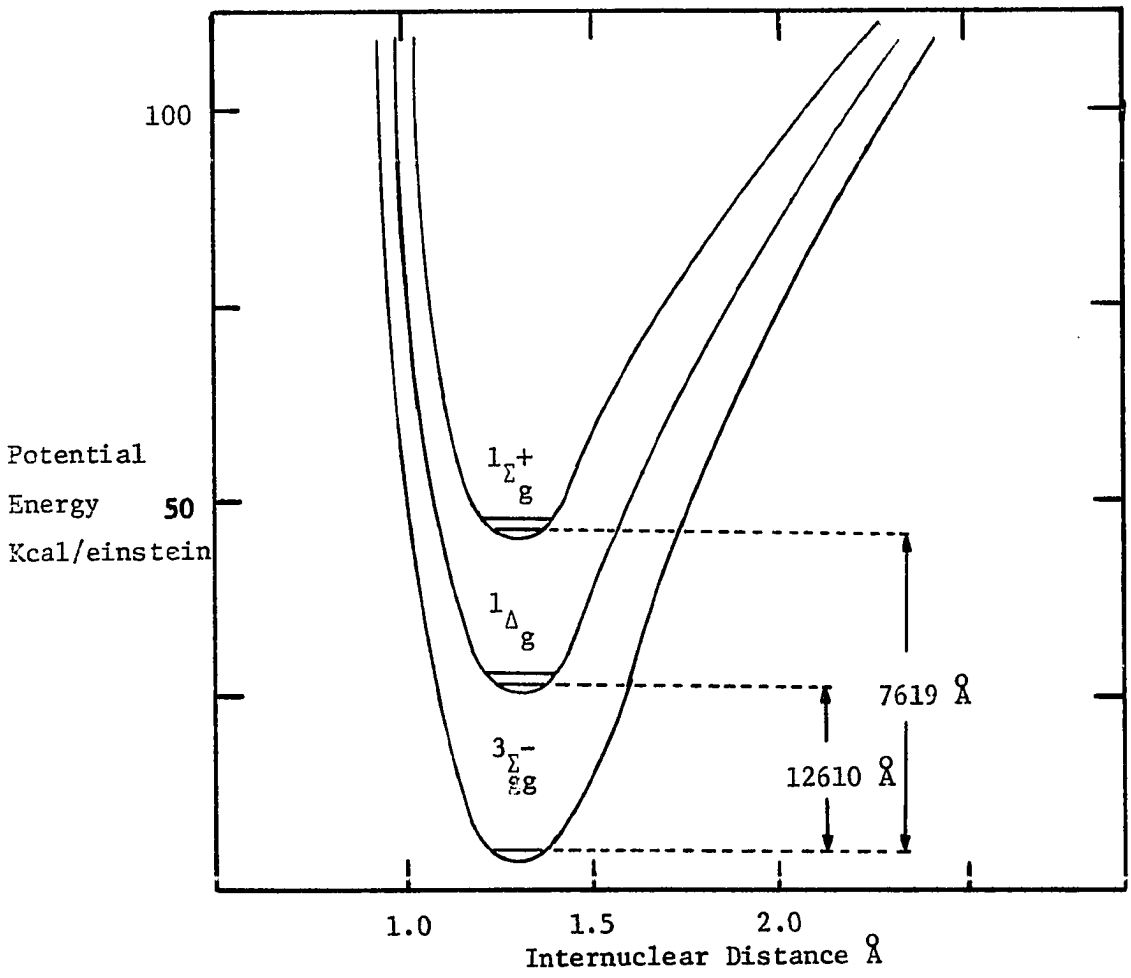


Figure 3. Potential Energy Curves for Oxygen (After Ogryzlo).

hypobromite. This method came from the studies of "red luminescence" observed when chlorine gas was bubbled through an alkaline solution of hydrogen peroxide. Spectroscopic research by Bowen and Lloyd, Khan and Kasha, Ogryzlo, et. al., established that the emission was due to the formation of singlet oxygen in the following reaction:

$$NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + {}^1O_2$$

b. reaction of potassium superoxide with water. Khan [21] reported that this method could be a favorable source for $^1\Sigma_g^+$ production. Potassium superoxide crystals are ionic lattices of K^+ and O_2^- ions. Therefore, the formation of singlet oxygen is assumed on the basis of a one-electron transfer reaction:

$$O_2^- \longrightarrow {}^1O_2 + e^-$$

The detailed nature of this chemical reaction is not clearly understood.

c. thermal decomposition of arylperoxide. This reaction probably favors the production of $^1\Delta_g$.

d. highly exothermic thermal and photochemical reactions of ozone could give rise to electronically excited molecular oxygen. This reaction is of considerable importance in atmospheric chemistry:

$$O_3 + h\nu \longrightarrow {}^1O + {}^1O_2$$

The wavelength at which this reaction can give $^1\Delta_g$

is approximately 3100 Å.

2. Physical Methods [17,37,50]

   a. photosensitization by visible or near ultra-violet light absorption. This process is considered a physical one, as the formation of singlet oxygen is produced by energy transfer from the excited sensitizer to normal oxygen. Most sensitizers favor $^1\Sigma_g^+$, and only with infrared sensitizers could $^1\Delta_g$ be exclusively produced.

   b. electrical discharge through a stream of gaseous oxygen. The products of an electric discharge through molecular oxygen contain an appreciable amount, 10-20%, of singlet oxygen. Scrubbing the mixture through water will eliminate O_2 ($^1\Sigma_g^+$) since this singlet state is easily quenched by water molecules. On the other hand, O_2 ($^1\Delta_g$) seems to be immune to deactivation by water molecules.

The detection of the presence of singlet molecular oxygen in a system may be affected by direct observation if concentration permits; otherwise, indirect detection by the result of singlet oxygen reactions should be performed. The useful detection methods are [17,50]:

Luminescence spectroscopy
Electron paramagnetic resonance
Mass spectroscopy
Chemical scavenger
Calorimetric

The Role of Singlet Molecular Oxygen in Photosensitized Oxidation

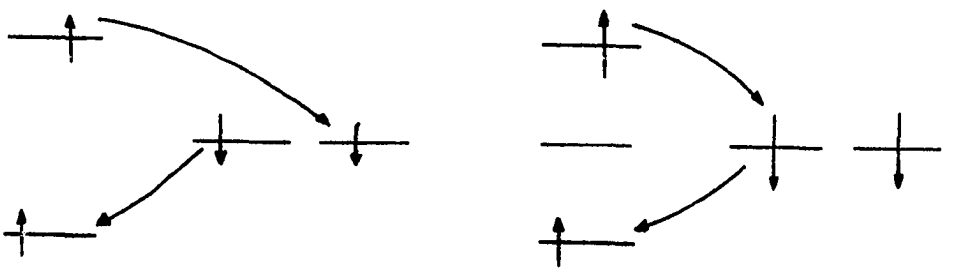
Because of the importance of singlet molecular oxygen in photosensitized oxidation, a more extensive review will be presented. The mechanisms of the formation of singlet molecular oxygen in photosensitized reactions, which Kautsky proposed and which now appear to be correct, are as follows [22]:

$Sens \xrightarrow{h\nu} {}^1Sens$	Excitation of sensitizer to an excited singlet state.
${}^1Sens \longrightarrow {}^3Sens$	Intersystem crossing of excited sensitizer to its lowest triplet state.
${}^3Sens + {}^3O_2 \longrightarrow Sens + {}^1O_2$	Formation of excited singlet oxygen, sigma or delta, by energy transfer to ground state oxygen.
${}^1O_2\ ({}^1\Sigma_g^+ \text{ or } {}^1\Delta_g) + A \longrightarrow {}^3O_2$	Reaction, deactivation, of singlet oxygen with molecule A.

A comparison of oxygenated products obtained from sensitized photooxygenation, with those formed under reaction conditions where singlet oxygen molecules were known to be present (H_2O_2 + NaOCl), gives evidence to the truism of the proposed scheme.

One of the basic assumptions in the Kautsky photooxygenation mechanism is that singlet oxygen molecules are generated by transfer of energy from the triplet state of the sensitizer to ground state oxygen. This energy transfer might seem odd since two triplet state molecules are lost and replaced by two singlet molecules. This mechanism is more understandable if viewed in terms of the simple orbital picture given in Figure 4.

Since no electron changes its spin in the transfer process this is a spin-allowed process, and either ${}^1\Delta_g$ or ${}^1\Sigma_g^+$ can be formed. Although these



(a) (b)

Note: in (a) $^1\Delta_g$ O_2 is formed.
in (b) $^1\Sigma_g^+$ O_2 is formed.

Figure 4. Molecular Orbital Diagram Describing the Transfer of Excitation Energy from a Triplet State Molecule to Molecular Oxygen (After Kearns and Kahn).

simple orbital diagrams are only meant to be suggestive, they do properly emphasize the fact that the energy transfer process is spin allowed and that the exchange of electrons between the sensitizer and molecular oxygen is essential. Based on the orbital diagram, any three of the low-lying singlet states of oxygen can be formed --two of these are deltas, 22 Kcal, and the other is sigma, 38 Kcal. However, this simple picture does not offer further guidance as to the relative rates at which these states are generated. The important conclusion resulting from a detail quantum mechanical analysis is that the quenching of high energy sensitizers --sensitizers with triplet state energies somewhat larger than 40 Kcal-- proceeds primarily by energy transfer to $^1\Sigma_g^+$, with energy transfer to $^1\Delta_g$ being slower by a factor of 10. Simple quenching of the excited sensitizer to its ground state, electronic state without energy transfer, is predicted to be even slower, probably by a factor of 10-100.

The energy transfer or quenching rate constant can be approximately calculated by use of the following relationship [22]:

$$k = k_o \, 0.15 \exp(-\Delta\varepsilon/4000)$$

where

k_o = rate constant expected if there were good matching of the purily electronic energies of the initial and final states of interest.

$\Delta\varepsilon$ = electronic excitation energy.

Kearns and Khan calculated the rate constants for the various processes of interest and the results are presented in Table IV [22].

TABLE IV

NUMERICAL VALUES OF RATE CONSTANTS OF VARIOUS PROCESSES*

Process	Calculated Rate Constant
$^3Sens + {}^3O_2 \longrightarrow Sens + {}^1O_2(^1\Sigma_g^+)$	10^{12}/sec.
$^3Sens + {}^3O_2 \longrightarrow Sens + {}^1O_2(^1\Delta_g)$	10^{11}/sec.
$^3Sens + {}^3O_2 \longrightarrow Sens + {}^3O_2$	10^{9}/sec.

*for a sensitizer with a triplet state energy of 60 Kcal located 4Å from oxygen. (Follows Kearns and Khan.)

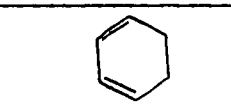
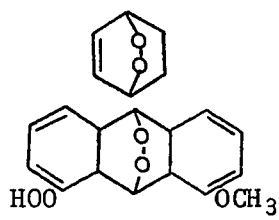
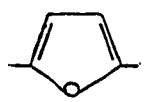
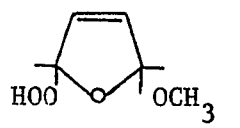
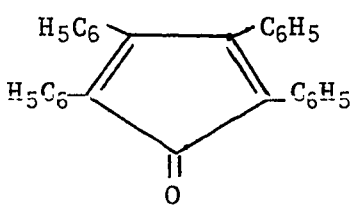
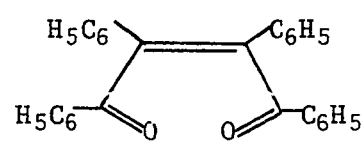
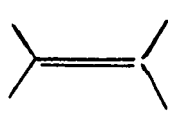
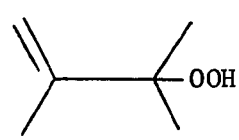
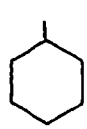
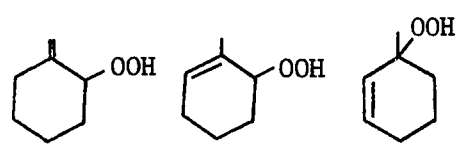
Since two colliding molecules in solution remain together for 10^{-10} sec., the results given in Table IV indicate that the energy transfer to either $^1\Delta_g$ or $^1\Sigma_g^+$ will occur with about a 100% efficiency on every collision between the triplet state sensitizer and oxygen. A simple application of the energy conservation leads to some interesting predictions regarding the variation in the relative generation rates of $^1\Sigma_g^+$ and $^1\Delta_g$ with sensitizer triplet energy. For a sensitizer with triplet state energies, E_t, less than 38 Kcal, but greater than 22 Kcal, only $^1\Delta_g$ oxygen can be generated by energy transfer so that the $^1\Sigma_g^+/^1\Delta_g$ ratio is zero. When E_t is larger than 38 Kcal, both $^1\Sigma_g^+$ and $^1\Delta_g$ can be generated and and theoretically the $^1\Sigma_g^+/^1\Delta_g$ should remain constant with increasing E_t. The result of this qualitative consideration leads to the curve given in

Figure 5, which shows how the relative magnitude of the $^1\Sigma_g^+/^1\Delta_g$ ratio varies with the triplet state energy of the sensitizer, E_t ranging from 25 to 70 Kcal.

Foote [13] studies the singlet oxygen reaction involving the addition of singlet oxygen to various dienes and aromatic hydrocarbons. Some of the acceptors and products formed on chemical oxygenation are shown in Table V.

TABLE V

ACCEPTORS AND THE PRODUCTS FORMED IN CHAMICAL PHOTOOXYGENATION REACTIONS

Compounds	Products
	
	
	
	
	

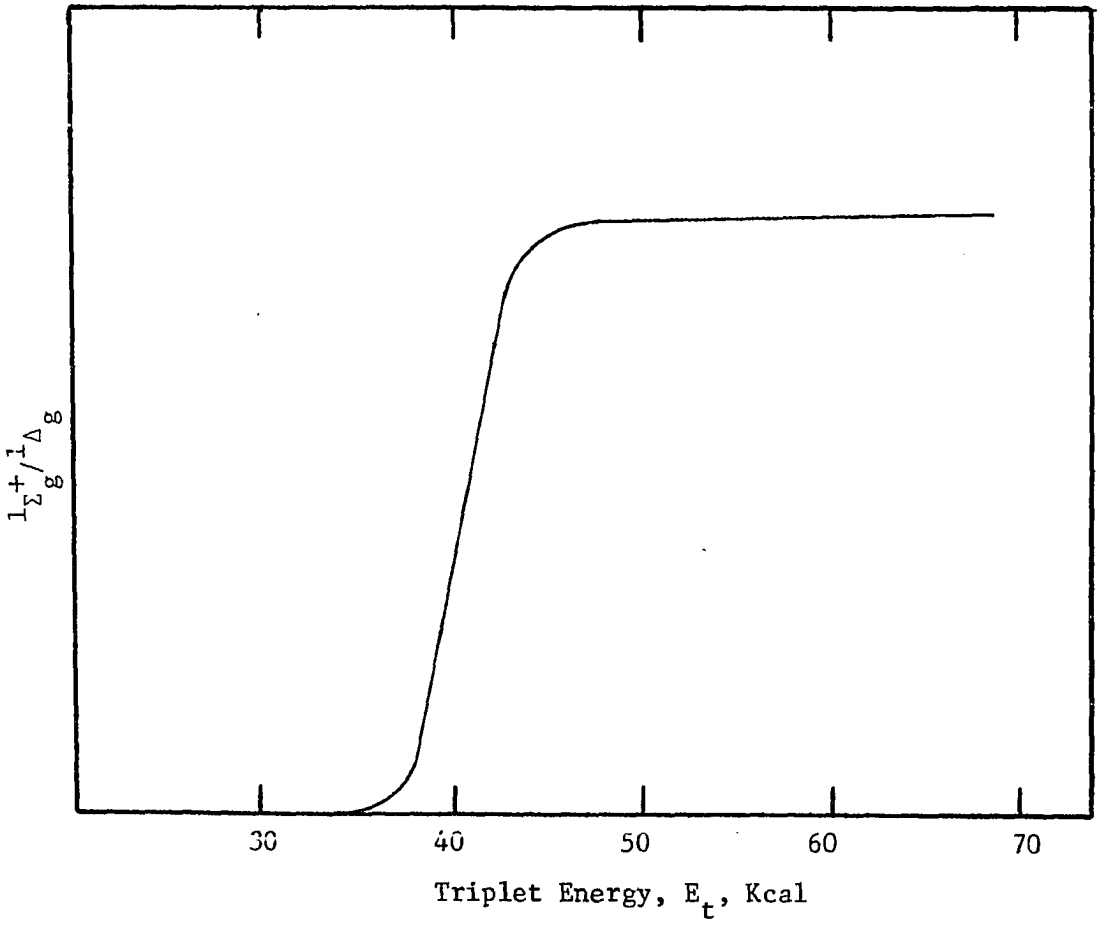


Figure 5. Variation in the $^1\Sigma/^1\Delta$ Ratio with the Sensitizer Triplet State Energy, E_t (After Kearns and Kahn).

Another type of reaction which is important in thermal autoxidation [22] and possibly some photooxidation reactions is the abstraction reaction:

$$RH + O_2 \longrightarrow R\cdot + HO_2$$

The studies of the reaction involving singlet molecular oxygen reveal the fact that the chemistry of ground state oxygen ($^3\Sigma_g^-$) is quite different from sigma or delta oxygen, and that reactivity of $^1\Sigma_g^+$ and $^1\Delta_g$ and the nature and course of reaction can be predicted by use of the State Correlation Diagram [15,22]. This diagram is constructed based on:

1. Thermochemical data, i.e. bond strengths, resonance energies, strain energies, used to located the ground state of the reactants relative to the ground state of the product.
2. Spectroscopic data used to locate the excited states of the reactants and products relative to their ground state.
3. Symmetry and spin selection rules applied to determine which state of the reactants will correlate with a particular state of the product.

The consequence of the non-crossing rule --states of the same multiplicity will not cross one another, is that the lowest singlet state of the reactant correlates with the lowest singlet state of the product, and the second lowest singlet state of the reactant correlates with the second lowest singlet state of the product, etc. Spin conservation requires that reactant triplet states correlate with triplet states of the products, and again the lowest triplet state of the reactant and the

product correlates with one another.

Using the addition of molecular oxygen to dienes and applying the State Correlation Diagram, Kearns and Khan concluded that ground state oxygen ($^3\Sigma_g^-$) was not expected to be reactive because this led to a triplet state of diene-O_2 complex which correlated with an excited triplet state of the product. From this it is generally correct to state that it is unlikely that triplet state oxygen will undergo concerted addition to any acceptor, unless the product has a very low-lying excited triplet state. Based on the State Correlation Diagram and Orbital Correlation Diagram, which can provide information on the initial behaviors of the states of the reactants and products, the following generalized conclusions were formulated:

1. Ground state oxygen($^3\Sigma_g^-$) is unreactive because the state of the complex associated with this state of oxygen, correlates endothermically with excited states of the product. $^1\Sigma_g^+$ oxygen is also unreactive in concerted cyclo-addition reaction. Exceptions are expected only if a very stable peroxide or radicals are formed.
2. $^1\Delta_g$ is generally reactive since this state of the complex usually correlates smoothly with the ground state of the peroxide.

The lifetime of sigma and delta singlet oxygen depends on the condition in which they are generated. The deactivation processes of these singlet states are primarily due to physical quenching and energy transfer [15,37,50]. Physical quenching occurs when an excited molecule collides with a normal molecule and its electronic excitation energy is

converted to vibrational and rotational energy, i.e. heat.

$$^1O_2(^1\Sigma_g^+ \text{ or } ^1\Delta_g) + M \xrightarrow{k_q} O_2 + M$$

It can also occur when excited oxygen molecule strikes the surface of the reaction vessel and is deactivated.

$$^1O_2 \xrightarrow{\text{wall}} O_2$$

An important characteristic of the delta state is that it is remarkably stable to physical quenching. Arnold, Kubo and Ogrylo [17] estimated that it could suffer 2×10^5 collisions with the wall of the vessel before deactivation. It is even more stable toward collisional deactivation by another molecule, and at least 10^8 collisions with normal O_2 molecules are required for deactivation of an oxygen ($^1\Delta_g$) molecule.

In a condensed fluid with hydrocarbon or water as quenchers, these quenching results suggest a lifetime of about 10^{-2} to 10^{-3} sec. for O_2, ($^1\Delta_g$). In a gaseous system the lifetime of O_2 ($^1\Delta_g$) is much longer on the order of 0.05-0.5 sec. in air at one atmosphere pressure.

The $^1\Sigma_g^+$ state is much less stable toward deactivation. It is estimated [16] that about 100 collisions with molecules of hydrocarbon or water are required for its deactivation. The product resulting from this quenching is presumably the $^1\Delta_g$ state. The lifetime of sigma oxygen in fluid solutions will be about 10^{-9} per second and the rate of quenching depends very much on the nature of the quencher, M. Thus Arnold, et. al. reported a quenching rate constant, k_q, ranging from 7×10^5 for helium; 1.5×10^6 for N_2, Ar and CO; to 6×10^8 for water --all expressed in liters mole^{-1} sec.$^{-1}$. Other investigators showed that compared to other quenchers, normal oxygen is a very inefficient quencher ($k_q = 6 \times 10^4$

liter mole^{-1} sec^{-1}) [17].

Photodynamic Action

Photodynamic action may be defined as the dye sensitized photooxidation of a biological substance with specific effects ranging from photokilling in the higher organisms, to alteration of biological function at the sub-cellular level [16]. The first quantitative studies on photodynamic action were made by Raab who found that low concentrations of acridines and other dyes, which had no effect on microorganisms such as paramecum in the dark, led to rapid death on illumination in the presence of oxygen [43]. These studies led to the important conclusion that almost any type of biological system, i.e. plants, animals, cells, viruses, biologically important molecules, can be sensitized and become subject to photodamage and destruction by appropriate dyes. Organic compounds in biological systems which undergo sensitized photoautoxidation include alcohols, aldehydes, amines, amino acids, carbohydrates, esters, indoles, ketones, nitrogen heterocyclics, olefins, nucleic acids, nucleosides, nucleotides, organic acids, phenols, pyrimidines, pyroles and steroid hormones [43]. It is very likely that compounds able to undergo autoxidation under a given set of conditions will also be oxidized in a dye-sensitized photo-reaction under the same conditions. It was further discovered that saturated and unsubstituted aliphatic compounds are resistant to sensitized photooxidation; whereas, benzoic and aromatic heterocyclic compounds are generally more susceptible to photosensitized oxidation. Benzene is not sensitive, but the introduction of amino or hydroxyl groups to the ring greatly increase the sensitivity of photooxidation, while the introduction of cyano, halogen, or nitro groups have little effect.

Hyaluronic acid, a high molecular weight linear polymer of alternating acetylglucosamine and glucoronic acid units, is depolymerized by illumination in the presence of appropriate dyes and oxygen [43]. Effective dyes include hemotoporphyrin and riboflavin. A variety of other dyes including acriflavin, acridine orange, crystal violet, eosin, methylene blue and neutral red also decrease the viscosity of hyaluronic acid solution on illumination in the presence of oxygen. This indicates that depolymerization takes place significantly.

In most cases, the intermediates in photodynamic action are short-lived and very reactive; hence, the reaction could proceed simultaneously by more than one mechanism with the predominant mechanism depending on the sensitizers, the substrates, and the reaction conditions [43].

The solvent in most photodynamic systems is water [43]. Some authors have suggested that water is split into O, OH, etc. as a primary reactant in sensitized photooxidation and photochemical reactions. However, later investigators, Rabinowitch, Moore, Holstrom and Oster, Kurtin, Latino and Sorig, concluded that photochemical splitting of water in photodynamic systems was unlikely. Other investigators have shown that water is not a primary reactant with photoexcited sensitizers, but can act as nucleophilic reagents attacking the electron deficient, oxidized substrate. There have been no systematic studies on solvent participation in photodynamic systems and thus for any given system the interaction of the solvent must be established.

Spikes and Straight summarized the reaction that have been shown to occur, or have been postulated to occur, by way of the triplet state in a photodynamic system. The reactions involved are tabulated in Tables VI

TABLE VI

PROBABLE ELEMENTARY REACTIONS OCCURING BY WAY OF THE TRIPLET, T_o, STATE

$^3A + T_o \longrightarrow {}^1A + S_o$	(1)
$^3A + T_o \longrightarrow {}^3A^* + S_o$	(2)
$^3A + T_o \longrightarrow \cdot(A\text{---}S)\cdot$	(3)
$^3A + T_o \longrightarrow \cdot A^-_{red} + \cdot S_{ox}$	(4)
$^oA + S_o \longrightarrow \cdot(S\text{---}A)\cdot$	(5)
$^oA + T_o \longrightarrow (S\text{---}A)^*$	(6)
$^oA + T_o \longrightarrow \cdot A_{ox} + \cdot S_{red}$	(7)
$^oA + T_o \longrightarrow \cdot A_{red} + \cdot S_{ox}$	(8)
$^oA + T_o \longrightarrow {}^3A + S$	(9)

Note: (After Spikes and Straight.)

and VII, where:

S_o and T_o = the singlet and lowest energy triplet state of sensitizer respectively;

^oA = any deactivating agent in the lowest singlet state;

(^3A) = molecular oxygen in its lowest triplet state;

(^1A) = the excited singlet state of oxygen, $^1\Delta_g$;

($^3A^*$) = vibrationally excited state of molecular oxygen, $^3\Sigma_g^-$;

$\cdot(A\text{---}S)\cdot$ = reactive sensitizer-oxygen intermediate, perhaps a peroxide or moloxide, a charge transfer complex;

TABLE VII

IMPORTANT REACTIONS IN SENSITIZED PHOTOOXIDATION, PHOTOOXIDATION AND PHOTOREDUCTION

$T_o + O_2 \longrightarrow S_o + O_2$	(10)
$T_o + O_2 \longrightarrow \cdot S_{ox} + \cdot O_2^-$	(11)
$T_o + R \longrightarrow S_o + R$	(12)
$T_o + R \longrightarrow \cdot S_{red} + \cdot R_{ox}$	(13)
$T_o + RH_2 \longrightarrow \cdot HS_{red} + \cdot HR_{ox}$	(14)
$T_o + S_o \longrightarrow \cdot S_{ox} + \cdot S_{red}$	(15)
$T_o + T_o \longrightarrow \cdot S_{ox} + \cdot S_{red}$	(16)
$\cdot S_{ox} + \cdot S_{red} \longrightarrow 2S_o$	(17)
$\cdot S_{ox} + R \longrightarrow S_o + R_{ox}$	(18)
$\cdot O_2^- + R \longrightarrow \cdot HO_2^-(H_2O_2) + \cdot R_{ox}$	(19)
$\cdot O_2^- + \cdot S_{ox} \longrightarrow S_o + O_2$	(20)
$\cdot S_{red} + O_2 \longrightarrow S_o + \cdot O_2^-$	(21)
$\cdot S_{red} + {}^1R_{ox} \longrightarrow S_o + R$	(22)

Note: (After Spikes and Straight.)

$(\cdot A_{red}^-)$ = semi-reduced radical of molecular oxygen;

$(\cdot S_{ox})$, $(\cdot S_{red})$ = semi-oxidized and semi-reduced sensitizer radicals;

$\cdot(S\text{---}A)\cdot$ = reactive radical produced by the excitation of a ground state complex between sensitizer and substrate;

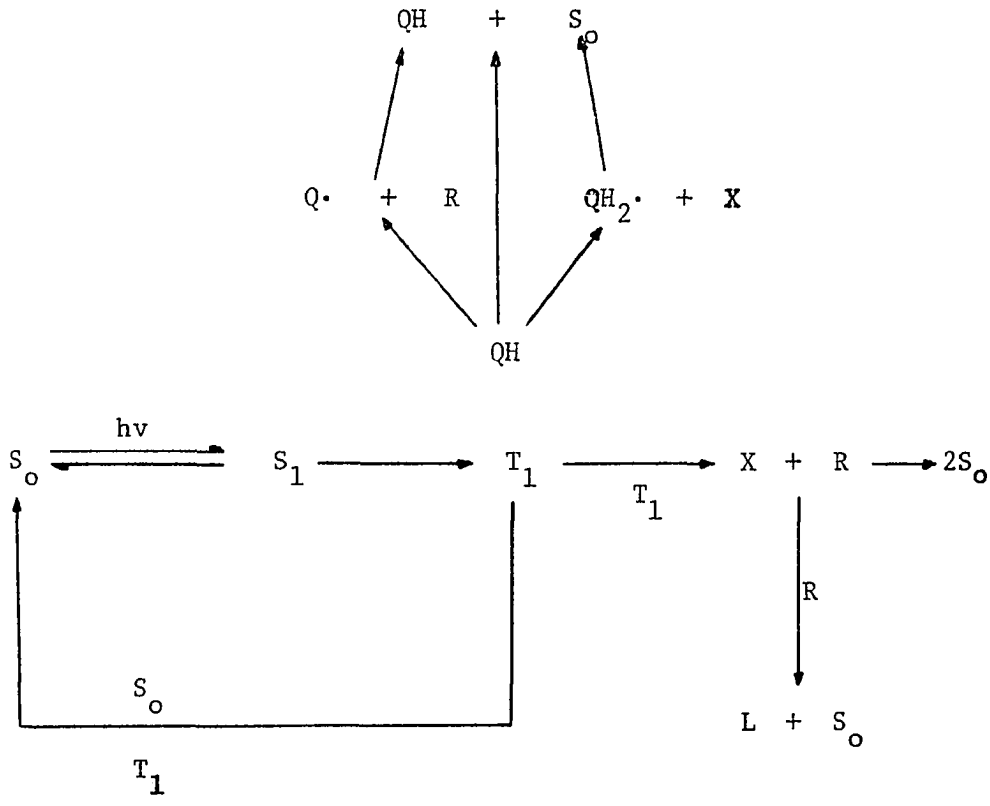
$(S\text{---}A)^*$ = reactive charge transfer complex between sensitizer triplet and substrate;

$(\cdot A_{ox})$, $(\cdot A_{red})$ = semi-oxidized and semi-reduced substrate radicals;

R	=	a weak anaerobic reducing substrate;
(RH_2)	=	strong anaerobic reducing substrate;
$(\cdot HS_{red})$	=	protonated form of the semi-reduced sensitizer;
$(\cdot HR_{ox})$	=	semi-oxidized reducing agent which can react with $(\cdot HS_{red})$ to product leuco dye.

Grossweiner [16] summarized the mechanism derived for sensitization by aqueous eosin under anaerobic conditions in Figure 6 and Table VIII. In the absence of reactive substrates the triplet state, T_1, is quenched by interacting with itself or with ground state molecules, S_o. Alternatively an electron transfer reaction may occur resulting in the formation of semi-quinone, R, and semi-oxidized intermediate, X, of phenoxyl structure. The dye radical may react together to restore the original dye to form equal parts of the colorless leuco, L, and the dye. The high electron affinity to triplet eosin is illustrated by its ability to oxidize many kinds of aromatic molecules and even hydrogen peroxide. The mechanism in Figure 6 may be modified by intermolecular interactions, such as aggregation or complexing, which are likely to be significant in photodynamic systems. Table VIII summarizes the known processes of this type involving the triplet state.

The presence of molecular oxygen introduces additional complications to the mechanism of the primary sensitization reactions. It is possible that oxygen attacks the substrate only after the latter has been partially oxidized by the excited dye. Molecular oxygen may act as a carrier of excitation energy or an oxidizing potential from the excited dye molecule to the substrate. The effective oxidizing entity might be a type of dye-oxygen complex. When oxygen is present the reduced dye will be restored



Note: S_o = excited dye; S_1 = first singlet; T_1 = lowest triplet state; R = semi-quinone; X = semi-oxidized eosin; L = leuco base; QH = reactive substrate; Q· = initial oxidation product; QH_2· = initial reduction product

Figure 6. General Mechanism For Photosensitization by Aqueous Eosin Under Aerobic Conditions.

TABLE VIII

INTERACTIONS THAT MODIFY TRIPLET EXCITATION AND DECAY PROCESS

Triplet Energy Transfer

$$T_1^d + S_o^a \longrightarrow S_o^d + T_1^a$$

T-T Annihilation (P Type Delayed Fluorescence)

$$T_1 + T_1 \longrightarrow S_1 + S_o \longrightarrow 2S_o + h\nu$$

E-Type Delayed Fluorescence

$$T_1 \xrightarrow{\text{heat}} S_1 \longrightarrow S_o + h\nu'$$

Biphotonic Sensitization

$$T_1 + h\nu \longrightarrow T^* \xrightarrow{QH} S_o + Q'$$

Biphotonic Ionization

$$T_1 + h\nu \longrightarrow T^* \xrightarrow{QH} S_o + QH^+ + e^-$$

Excitation of Dye Aggregates

$$(\text{--}S_oS_oS_oS_o\text{--}) + h\nu \longrightarrow (\text{--}S_oS_oS_1S_oS_o\text{--}) \longrightarrow (\text{--}S_oS_oT_1S_oS_o\text{--})$$

Excitation of Bound Dye

$$(S_o)_b + h\nu \longrightarrow (S_1)_b \xrightarrow{(S_o)_b} (T_1)_b + (S_o)_b$$

Excitation of Charge Transfer Complex

$$(S_o^+\text{-}QH^-) + h\nu \longrightarrow (S\text{-}QH)^* \longrightarrow (T_1\text{-}QH)$$

Note: T_1^d, T_1^a = donor and acceptor triplet state;

S_o^d, S_o^a = donor and acceptor singlet state.

(After Grossweiner.)

by its reaction with oxygen while the substrate may be further oxidized. Table IX summarizes the overall dye sensitization processes in the presence of oxygen. The free radical chain reaction of Gollnick and Schenck, reaction (b) which yields peroxide and restoration of the sensitizer, is applicable only when the substrate is free to migrate.

Beginning with the pioneering works of Kautsky in 1937, a number of experiments have shown that photosensitized oxidation can take place even when the dye and the substrate are separated. The oxidation entities proposed by different workers that explain the reaction mechanism include excited singlet molecular oxygen [22], ground state oxygen with high vibrational energy, and the radical ion, $O_2^{-}\cdot$. The formation of the dye oxygen or moloxide has received the strongest support from the work of Schenck. Reaction (e), Table IX, indicates the moloxide mechanism.

Bourdon and Schnuriger [6] pointed out that the actual path of an oxygen sensitizer activation depends on the specific dye and the reaction conditions. For example, reaction (a) in Table IX requires the suppression of triplet deactivation by oxygen to be effective. Finally, it should be mentioned that the nature of the substrate also determines whether the sensitizer-substrate or sensitizer-oxygen interactions are important in the initial reaction.

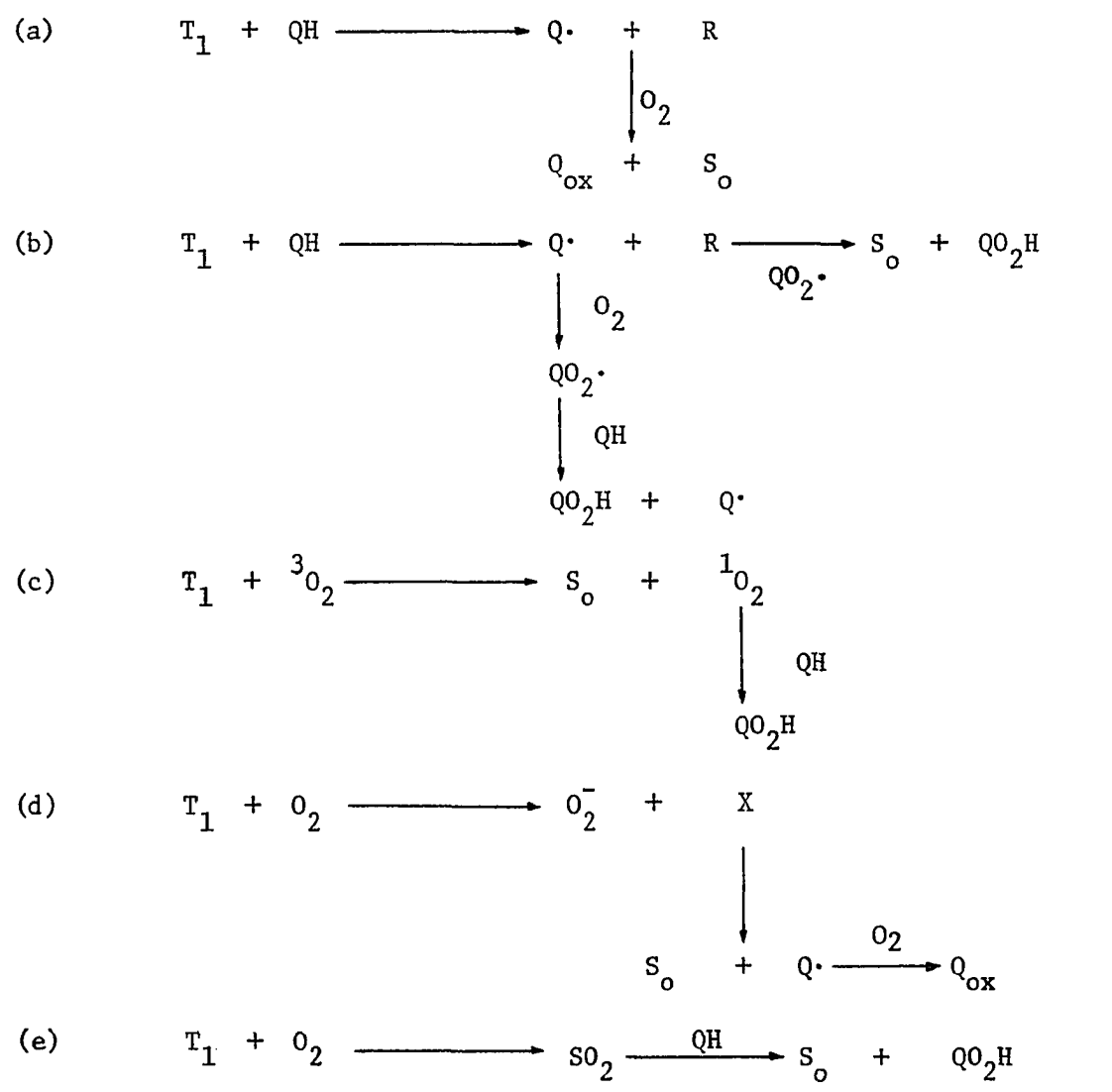
The mechanistic consideration review involves only the first molecular steps, while the observable effects almost certainly depend on the subsequent chemical reaction of the initial radical products and other factors in the system, e.g. solvent participation, temperature, etc.

Photosensitized Oxidation "At a Distance"

A sensitized photoreaction occuring in the solid state can be

TABLE IX

DYE SENSITIZATION PROCESSES IN THE PRESENCE OF OXYGEN



Note: Q· = free radical resulting from one-electron oxidation;

Q_{ox} = oxidation product of unspecified type;

QO_2· = peroxy radical;

QO_2H = stable products of peroxide (b), or adduct (c), (e) types.

(After Grossweiner.)

governed or modified by the following [6]:

1. Factors affecting the nature of the state of the sensitizing agent.
   a. rigidity of the medium or adsorption which prevent thermal deactivation processes and depopulation by impurities and oxygen.
   b. dimerization of the sensitizer favored by adsorption on solid surface or on macromolecules.
   c. modification of the electronic structure of the sensitizer by adsorption.
2. Factors affecting the photosensitization process, i.e. the relation existing between the sensitizer and the sensitized molecule. This process will be dependent upon:
   a. energy transfer;
   b. charge transfer;
   c. diffusion of activated small molecules or activated species. The role and the importance of these factors have been discussed quite extensively by several authors [6,8,35,47].

A remark should be made concerning the importance of oxygen as a quencher of the triplet state, and the permeability of the polymeric matrix for this gas. A low permeability toward oxygen will consequently decrease the quenching of the triplet, enhance its lifetime, and allow the phosphorescence to be observed; however, it will prevent the occurrence of photosensitized oxidation which can happen only in permeable polymers.

The photosensitized reaction in the solid state is more favorable due to the fact that the concentration of the sensitizer can reach locally high values with the subsequent formation of dimers, aggregates and microcrystals. These various states of association, i.e. dimers, aggregates, etc., of the sensitizer molecules are highly favorable to various electronic processes, such as the energy migration in molecular crystal by exciton mechanism.

The two types of well known phenomena in which the reactions occur "at a distance" are photodynamic action and the dye-photosensitized tendering of textile fibers. Generally speaking, when a dye is in contact with or in the neighborhood of an organic compound, on a solid or semisolid medium its illumination in the presence of oxygen, air, very often produces a photochemical transformation of the organic compound. This is sometimes accompanied by simultaneous bleaching of the dye. In most cases these are oxidation-reduction reactions. Their nature depends on the physical and chemical properties of the sensitizer, on the organic compound and on the relationship which exists between them, such as distance, associative forces, etc. As these reactions take place in the presence of air, the final result is oxidation, although intermediate steps may occur without oxygen participation which involves the reduction of one of the two reactants. The nature of the reaction is dependent upon the local oxygen pressure, that is upon the degree of excess oxygen to the excited molecules and to eventual activated intermediates. This is quite understandable if the reaction mechanisms which indicate interactions between oxygen and the triplet state sensitizer or activated substrate molecules are considered.

The sensitizer responsible for these reactions has been reviewed

earlier in this chapter. Evidence shows that the sensitizers which are effective in the degradation of textile fibres --natural or artifical: cotton, wool, nylon, silk, etc.-- do not belong necessarily to the same types of dyes which have been found to sensitize the photodynamic action

Egerton's experiment, as has been mentioned earlier, showed the evidence of the phototendering of cellulose fibres by various sensitizers, pigments and dyes. It was Kautsky who first demonstrated that a photosensitized oxidation reaction could occur where sensitizer and oxidizable compounds were held at a distance from each other. He used different dyes absorbed on the surface of solid silica gel or aluminium oxide gel, and suitable oxidizable organic compounds, leuco malachite green, absorbed on larger particles of silica gel as acceptors. When this mixture was irradiated in the presence of oxygen, a blue color was observed. This resulted from the photoxensitzed oxidation of leuco malachite green with production of the corresponding dye. The reaction is dependent on oxygen pressure as can be seen in Table X.

TABLE X

EFFECT OF OXYGEN PRESSURE ON THE COLORATION OF LEUCO MALACHITE GREEN UNDER ILLUMINATION

Oxygen Pressure 10^{-4} mm Hg	Time of Illumination, Minutes	Coloration of Malachite Green Produced
0.4	10	none
1.4	10	none
12	10	faint
18	10	strong blue
24	10	faint
40	10	none

*(After Kautsky)

From this experiment Kautsky concluded that oxidation was performed by oxygen in its excited singlet, which was able to diffuse from the sensitizer to the acceptor. The observations indicate that an optimum oxygen pressure, concentration, determines the efficiency of the process. This phenomenon is inherent with the nature of photochemical reactions at concentrated solutions, where the nominal concentration quenching reaction becomes the controlling factor in the overall reaction. Hence, higher oxygen pressures are responsible for the deactivation of the excited oxygen by collisions. The adverse effect of the reactants, to the extent of the reaction, will be discussed in the following section.

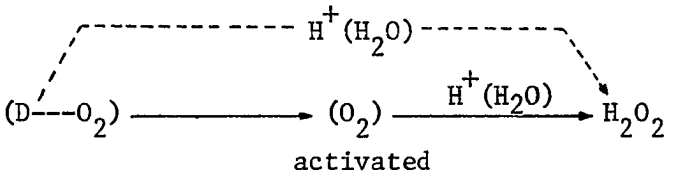
Rosenberg and Humpries [41] studied the participation of excited oxygen in a chemiluminescence reaction within a system consisting of an absorbate of purified acriflavin on silica gel. They concluded that the oxidation entities were either the singlet excited O_2, $^1\Sigma_g^+$, or the vibrationally excited oxygen, O_2^*, in the ground electronic state. Evidence pointed with high probability to the role of the O_2^* in the reactions investigated. The presence of singlet excited oxygen, $^1\Delta_g$, had to be ruled out as observations indicated that the oxygen consumption was inhibited by CO_2, argon, N_2O and CH_4. This is in contradiction to the nature of O_2, $^1\Delta_g$, which is practically invulnerable to deactivating collisions [15,50].

The oxidizing entities --excited singlet oxygen, O_2^*, O_2^- and H_2O_2, which are responsible for the photosensitized oxidation at a distance, have been studied by many investigators. The results as appear in Table XI can be used to postulate the existence of oxidation species in photosensitized oxidation in the solid state. This summary is based on the understanding that various species have the ability to diffuse over a

certain distance from the sensitizer. In conclusion, it is necessary to note that the present knowledge of the mechanism of photosensitization in an organic solid is based on reactions in solutions, and many of the theories discussed are essentially extrapolative.

TABLE XI

POSTULATED NATURE OF OXIDIZING ENTITIES IN PHOTOSENSITIZED OXIDATION IN THE SOLID STATE



intermolecular distance	d<10 Å	10 Å<d<1μ	d∿ mm (up to 8mm)
condition of observation	solution	low oxygen pressure	presence of water
	absorbed state	no water	
		permeable matrix	

*(After Bourdon and Schnuriger.)

Mechanistic and Kinetic Studies on Sensitized Photooxidation

Reaction Mechanism

Some of the reaction pathways and mechanisms of the photosensitized oxidation under particular conditions have been reviewed earlier. This section will cover the generalized form of the reaction mechanism.

There are two mechanisms [19] by which oxygen is incorporated into photochemical oxidation reactions. The first is the Blackstrom mechanism, or photosensitized oxidation mechanism. Its main feature is abstraction of hydrogen by the triplet state sensitizer followed by oxidation of the newly created radical.

$$\text{Sens} \xrightarrow{h\nu} \cdot\text{Sens}\cdot$$

$$\cdot\text{Sens}\cdot + \text{AH} \longrightarrow \cdot\text{Sens-H} + \text{A}\cdot$$

$$\text{A}\cdot + \text{O}_2 \longrightarrow \text{AOO}\cdot$$

$$\text{AOO}\cdot + \text{AH} \longrightarrow \text{AOOH} + \text{A}\cdot$$

$$\text{AOO}\cdot + \cdot\text{Sens-H} \longrightarrow \text{AOOH} + \text{Sens}$$

Examples of photosensitized reactions that follow this mechanism are found in the oxidation of secondary alcohols to hydroxy hydroperoxide, which in aqueous media decompose to form ketone and hydrogen peroxide.

$$\text{R}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}=\text{R}' \xrightarrow{h\nu, O_2} \text{R}-\underset{\text{OOH}}{\overset{\text{OH}}{\text{C}}}-\text{R}' \xrightarrow{H_2O} \text{R}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{R}' + \text{H}_2\text{O}_2$$

The secondary mechanism, that of photosensitized oxygen transfer, involves the direct combination of the substrate with oxygen. There are two proposals regarding the state of the oxygen involved. Schenck [14,19], the main contributor to the field of photosensitized oxygenation reactions, strongly advocates that the interaction between an electronically excited sensitizer, triplet, and oxygen should result in a chemical addition reaction rather than in a physical energy transfer.

$$\text{Sens} \xrightarrow{h\nu} \cdot\text{Sens}\cdot\text{(triplet)}$$

$$\cdot\text{Sens}\cdot + \text{O}_2 \longrightarrow \cdot\text{Sens-O-O}\cdot$$

$$\text{A} + \cdot\text{Sens-O-O}\cdot \longrightarrow \text{AO}_2 + \text{Sens}$$

Foote [13,19] favors the idea of singlet oxygen being the sole agent in the energy transfer step:

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^{*}(\text{triplet})$$

$$O_2(\text{triplet}) + \text{Sens}^{*}(\text{triplet}) \longrightarrow O_2(\text{singlet}) + \text{Sens}$$

$$A + O_2(\text{singlet}) \longrightarrow AO_2$$

Chemical reactions of this type, in which the sensitizer is a dye such as Bengal Red or fluorescein, include the oxidation of dienes, furans and substituted olefins. The formation of hydroperoxide in photosensitized oxygen-transfer reactions, that follow the Schenck type of mechanism, occur only when hydrogen is present in the allylic position of the olefin. Oxygen always becomes attached to one carbon of the double bond and then shifts to the allylic position.

$$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}(H) \xrightarrow[\text{Sens}]{h\nu, O_2} \overset{1}{C}(OOH)-\overset{2}{C}=\overset{3}{C}$$

Kinetics

The kinetics of photooxygenation, direct and indirect have been studied and discussed by many investigators [8,9,14,15,17,26,31,51]. Before reviewing the kinetics of particular photochemical reactions, it is deemed necessary to discuss the fundamentals of photochemical reaction rates.

In the beginning of this chapter, the following formula was developed:

$$\frac{dn_p}{dt} = \alpha \frac{I}{h\nu} n_A$$

This indicates that under constant conditions, i.e. light intensity, wavelength, geometry of the reactor, temperature; the formation of reaction

products or the disappearance of A per unit time is proportional to n_A,

$$\frac{dn_p}{dt} = -\frac{dn_A}{dt} = kn_A$$

which is first order kinetics.

It is acknowledged that the variables of absorbed light intensity and wavelength, or energy input, are unique to the study of photochemical reactions [8]. The effect of continuous and intermittent illumination on the rates of a reaction give important information concerning the reaction mechanism. The intensity dependence of the production rate of a product can help to establish whether a product is formed in a primary or secondary reaction. Since only one quantum is absorbed to initiate the primary process, the rates of primary processes are directly proportional to the absorbed light intensity, I. The quantum yields of primary products are independent to I, since:

$$\phi_A = \frac{dn_A}{dt} \Big/ I_a$$

where:

$$I_a = E_t Q_m \lambda / Vhc$$

E_t = total energy incident on the system per second.

Q_m = $1-10^{-\varepsilon cl}$ = fraction of energy absorbed by molecule.

V = volume of irradiated system

but,

$$\frac{dn_A}{dt} = \alpha \frac{I_a}{h\nu}$$

hence:

$$\phi_A = \alpha \frac{n_A}{h\nu}$$

Rates of products formed in secondary reactions usually show something other than first power dependence on I. In general, bimolecular termination by a reaction involving active chain-carrying species results in rate proportional to $I^{\frac{1}{2}}$. This relationship can be observed from the study of the photochemical formation of HBr from Br_2 and H_2 [8], where it is found that:

$$\frac{d[HBr]}{dt} \propto I_a^{\frac{1}{2}}$$

In a simple first order reaction one would expect that the reaction rate constant, k, will not be affected by the initial concentration. Various photochemical reactions are generally assumed to follow unimolecular reaction, although in the strictest sense they might be considered bimolecular reactions between a molecule and a quantum of light. Lindeman suggested a reasonable scheme for this apparent unimolecular reaction in terms of the collision theory [8].

The molecules, A, are activated by collision with other molecules of A to an excited state, A^*.

$$A + A \xrightarrow{k_2} A^* + A \qquad (1)$$

The formation of products can occur only through A^*.

$$A^* \xrightarrow{k_2} \text{Products} \qquad (2)$$

A^* can be deactivated by bimolecular reaction:

$$A^* + A \xrightarrow{k_{-2}} 2A \qquad (3)$$

If (1) and (3) are faster than (2), then the rate will be determined by:

$$-\frac{d[A]}{dt} = k_1[A^*] \qquad (4)$$

A^* is derived from the reaction sequence based on the assumption that its rate of formation is equal to its rate of destruction, $d[A]/dt = 0$. The

rate of reaction is given by:

$$- \frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_1 + k_{-2}[A]} \tag{5}$$

When $k_{-2}[A] >> k_1$ in the presence of high A concentrations, (5) becomes a first order reaction:

$$- \frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-2}} \tag{6}$$

At low A concentrations, $k_{-2}[A] << k_1$ the reaction appears to become second order as the rate of A disappears:

$$- \frac{d[A]}{dt} = k_2 [A]^2 \tag{7}$$

Assuming that the reaction is first order, the rate constant, k_I, evaluated experimentally, is shown as:

$$k_I = \frac{k_2 k_1 [A]}{k_1 + k_{-2}[A]} \tag{8}$$

Rearrangement of equation (8) gives the following relationship:

$$\frac{1}{k_I} = \frac{1}{k_2 [A]} + \frac{k_{-2}}{k_1 k_2} \tag{9}$$

Plotting the values of $1/k_I$ vs $1/[A]$ will give a straight line with a slope and an interception equal to $1/k_2$ and $k_{-2}/k_1 k_2$ respectively.

The above relationship shows that the overall rate constant, k_I, measured experimentally, increases as the substrate concentration, [A], increases, provided the assumptions hold for the process involved.

The temperature dependence of experimental rate data usually can be presented by the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where:

k = the reaction rate constant;

A = pre-exponential factor or frequency factor;

E_a = experimental activation energy;

T = absolute temperature in ^{o}K, and

R = gas constant.

Reaction rate theories have been developed which give theoretical significance to the various terms in this equation. Two such theories are in common use today --the collision theory and the transition state theory. Extension use of the collision theory has been stimulated by the simplicity of its application although it is recognized to be a very incomplete and an inaccurate picture of the true nature of chemical reactions. Many limitations of the older collision theory are overcome by the transition state theory.

The reaction rate dependency on temperature can be best described by the values of $e^{-E_a/RT}$ for various E_a and temperature as presented in Table XII. For a given E_a, the fraction of collisions which have energies greater tha E_a increases as the temperature rises, reflecting the usual increase in temperature. It can be seen that for a given E_a, the higher E_a, the greater the rate of increase of $e^{-E_a/RT}$, and the reaction rate with temperature increase. Thus a reaction rate with E_a = 5 Kcal/mole, which is the range for photooxygenation reactions, will increase by a factor of approximately 2.95 x 10 for a temperature rise of 200^{o}, from $300^{0}K$ to $500^{o}K$. While a reaction with E_a = 25 Kcal/mole increases by 1.94×10^{7} for the same temperature change, neglecting the temperature dependence of A.

TABLE XII

VALUES OF $e^{-E_a/RT}$ FOR VARIOUS E_a AND TEMPERATURE VALUES[8]

E_a, Kcal/mole	Temperature, ^oK			
	300	400	500	600
0	1	1	1	1
2	3.5×10^{-2}	8.1×10^{-2}	1.3×10^{-1}	1.9×10^{-1}
5	2.2×10^{-4}	1.9×10^{-3}	6.5×10^{-3}	1.5×10^{-2}
10	5.2×10^{-8}	3.4×10^{-6}	4.3×10^{-3}	2.8×10^{-4}
25	6.2×10^{-19}	2.2×10^{-14}	1.2×10^{-11}	7.9×10^{-11}
50	2.8×10^{-37}	4.8×10^{-28}	1.4×10^{-22}	6.2×10^{-19}

The aforementioned discussion is a review of temperature dependence of reaction rate constant. In contrast to the nature of reaction rate which is generally temperature sensitive, the rate of formation or the quantum yield of some products is insensitive to temperature change. Evidence indicates that most primary dissociative processes are slightly affected by temperature. A remarkable difference of photochemical reactions with thermal reaction where only high energy molecules react, is that molecules, which absorb photons and undergo photochemical changes, have the usual distribution of thermal energies in their ground state. The increase in thermal energies encountered in the temperature range of the usual photochemical study is small compared to the magnitude of the electronic excitation induced by the absorbed quantum. For example, a

rise in temperature for acetylaldehyde, absorption peak of 2900-3000 Å from 20^{o} to 220^{o}C, causes an increase in average thermal energy of about 3 Kcal/mole; while the usual electronic excitations are near 100 Kcal/mole --2.859×10^{5}: 2900 = 99 Kcal/mole. Therefore, in most cases thermal energies are unimportant in determining the mode and efficiency of photodecomposition. Temperature dependence of a primary process may be significant in certain cases; for example, where inadequate energy for bond rupture is available from the absorbed quantum, or when there is an activated energy for the dissociation of the light activated molecule. As will be shown later, the primary photooxygenation process is relatively insensitive to temperature change.

Another aspect of photochemical kinetics that should be examined is the effect of a gaseous or condensed phase on the system. A brief review of the reaction kinetics in condensed systems will be presented here.

The liquid state is not understood in the same detail as are the gaseous and solid states. In gaseous states the interaction between the individual molecules are usually relatively unimportant. The molecules therefore, behave largely in a random manner and can be treated in terms of the kinetics theory, which deals with such randomness. Solids, having a regular structure can also be treated in a satisfactory manner. Liquids, on the other hand, have neither a completely random nor a completely regular structure and their theoretical treatment is consequently much more complicated. The rate constants for a given reaction between neutral free radicals and molecules do not usually differ greatly in the two phases. Certain thermal reactions of ions and photochemical primary processes involving ion formation and electron transfer, unknown to the gas phase,

become energetically favorable and are important in solution of high dielectric constant. If homogeneous light absorption is maintained, then the liquid phase systems are usually less complicated by wall-reactions, than the gas phase counter parts, because of much lower diffusion rates for the liquid systems.

The most striking of the effects encountered in solution-phase photochemistry is the so called "cage effect", or Franc-Rabinowitch [3,5] effect. In the case of photochemical reactions in solutions, a pair of free radicals produced initially may, because they are caged in by surrounding solvent molecules, recombine before they can separate from one another. This phenomenon is known as primary recombination, as opposed to secondary recombination which occurs after the free radicals have separated from one another. As a result of this cage effect, the quantum yield of products derived from free radical formation are often significantly lower than the analogous gas phase experiments.

Reaction Kinetics of Photooxidation

Some quantitative analyses of the kinetics type II, direct and indirect photooxygenation reactions, have been made by several investigators [13,14,15,17,28,42]. The analyses deal with the photooxygenation of 2,5 dimethyl furan and allyl-thiourea sensitized by xanthene dyes, and chlorophyll, respectively, and with direct photooxygenation of anthracene and 9,10-diphenylanthracene. Gollnick [14,15,17] conclude that there is no need to postulate an intermediate complex formation. The formation can be replaced by singlet oxygen and this leads to the following reaction sequence:

$^1S_o + h\nu \xrightarrow{I_{abs}} {}^1S_1$	Absorption
$^1S_o \xrightarrow{k_2} {}^1S_1 + h\nu$	Fluorescence
$^1S_1 \xrightarrow{k_3} {}^1S_o$	Internal conversion
$^1S_1 \xrightarrow{k_4} {}^3S_1$	Intersystem crossing to the triplet state
$^3S_1 \xrightarrow{k_5} {}^1S_o$	Intersystem crossing to the singlet state
$^1S_1 + {}^3O_2 \xrightarrow{k_6} {}^1S_o + {}^1O_2$	Energy transfer
$^3S_1 + {}^3O_2 \xrightarrow{k_7} {}^1S_o + {}^1O_2$	Formation of singlet oxygen
$^1O_2 \xrightarrow{k_8} {}^3O_2$	Deactivation of $^1O_2$
$^1O_2 + A \xrightarrow{k_9} {}^1(AO_1)_o$	Product Formation

where:

S = A in direct photooxygenation.

S = photosensitizer different from A in indirect photooxygenation reaction.

^1S_o, $^1S_1$, $^3S_1$ = singlet ground state, first excited singlet state and first triplet state of S, respectively.

^1A_o = singlet ground state of A.

$^1(AO_2)_o$ = singlet ground state of AO_2.

$^3O_2$ = triplet ground state oxygen.

$^1O_2$ = excited singlet oxygen, delta or sigma.

The quantum yield of the AO_2 formation is given by:

$$\phi_{AO_2} = \frac{[O_2]}{k_2 + k_3 + k_4 + k_6[O_2]}\left(k_6 + k_4 \frac{k_7}{k_5 + k_7[O_2]}\right)\frac{k_9[A]}{k_8 + k_9[A]}$$

If $k_8/k_9 << A$, or if substrate A is very reactive toward oxygen as in the case of 2,5 dimethyl furan, then the quantum yield, ϕ_{AO_2}, is equal to the singlet oxygen formation, $\phi_{1_{O_2}}$, given by:

$$\phi_{AO_2} = \frac{[O_2]}{k_2 + k_3 + k_4 + k_6[O_2]}\left(k_6 + k_4 \frac{k_7}{k_5 + k_7[O_2]}\right) = \phi_{1_{O_2}}$$

Based on the assumption that only triplet state sensitizers take part in the formation of singlet oxygen and at high oxygen concentration, $10^{-2} - 10^{-3}$ mole/liter, then $k_5 << k_7[O_2]$, $k_4 >> k_6[O_2]$ and the above equation reduces to:

$$\phi_{AO_2} = \frac{k_4}{k_2 + k_3 + k_4} = \phi_{3_{S_1}}$$

In other words, the quantum yield of the product formation determined at a high oxygen concentration equals the quantum yield of triplet sensitizer formation.

The quantum yield of product formation of photosensitized oxygenation reactions of substrate other than 2,5 dimethyl furan is given by the general equation,

$$\phi_{AO_2} = \phi_{1_{O_2}} \frac{A}{A + \beta}$$

with $\beta = k_8/k_9$ and $\phi_{1_{O_2}}$ given by the above relationship obtained from a 2,5 dimethyl furan photooxygenation reaction. Most substrates are less reactive than 2,5 dimethyl furan toward so that $A >> k_8/k_9$, which was used in the previous discussion, is not valid even at relatively large

concentrations. It is found that β is independent on the nature of the sensitizer, but slightly dependent on the solvent used. On the other hand, $^{\phi}1_{O_2}$ of the sensitizer remains practically unaffected by the change of solvents.

The change of β with a solvent may be due to either a change of the lifetime of singlet oxygen, $1/k_8$, or a change of the reactivity of the substrate toward singlet oxygen, k_9, or both.

The temperature dependence of photosensitized oxygentation reactions of several substrates has been studied by Schenck, Koch and co-workers [14]. Using Rose Bengal as the sensitizer and α-pinene as the substrate in different solvents, the quantum yields of photooxygenation drop to about 50% of the room temperature values when the temperature is lowered to -120°C (solvent A) or -140 to -150 (solvent D and C, respectively). (See Table XIII.)

TABLE XIII

TEMPERATURE DEPENDENCE OF SENSITIZED PHOTOOXYGENATION OF α-PINENE IN DIFFERENT SOLVENTS

Temperature, °C	O_2 Consumption, ml/min. Solvent			
	A	B	C	D
20	40	-	47	42
-30	39	-	47	42
-50	38	-	46	42
-70	35	38	45	41.7
-100	30	36	44	37.4
-120	20	26	33	32.6
-140	-	13	30	27
-150	-	8	20	-

Note: A = n-propanol;methanol;acetone = 2:2:1
B = propanol; methanol; acetone; propane = 2:2:1:1
C = n-propanol; methanol; propane; ether; petrol ether = 2:2:1:6:5
D = ether; ethanol; ethyl acetate = 3:4:4

The temperature coefficient, per $10^{o}C$, is thus about 1.005, showing that the activation energy of this particular photooxygenation is close to zero. (See Table XII.) With olefins, activation energies were determined to be between 1 and 5 Kcal/mole (Table XIV).

TABLE XIV

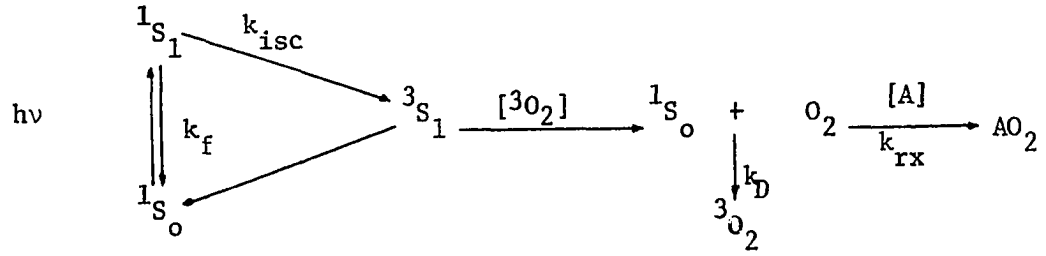
ACTIVATION ENERGIES OF THE TERMINATION STEP IN PHOTOSENSITIZED OXYGENATION REACTIONS

Substrate	Activation Energy Kcal/mole
2,5 dimethyl furan	0[a]
furan	0[a]
α-terpinene	0.5[a]
1,3 cyclohexadiene	1.1[a]
thiourea	1.5[b]
cyclopentadiene	2.4[a]
furfural	3.4[b]
isoamylamine	6.0[a]

Note: [a]sensitizer = Rose Bengal
[b]sensitizer = Methylene Blue

Young, et. al.[17] compared the reaction mechanisms and kinetics of photosensitized oxidation and direct photooxidation. Using 2-aryl furan as the substrate and Rose Bengal as the sensitizer, the reaction schemes are outlined as follows.

1. Photosensitzed Oxidation (indirect):



where:

k_{isc} = rate constant for intersystem crossing

k_f = rate constant of fluorescence

A = substrate

The kinetics for the disappearance of the arylfuran are represented by:

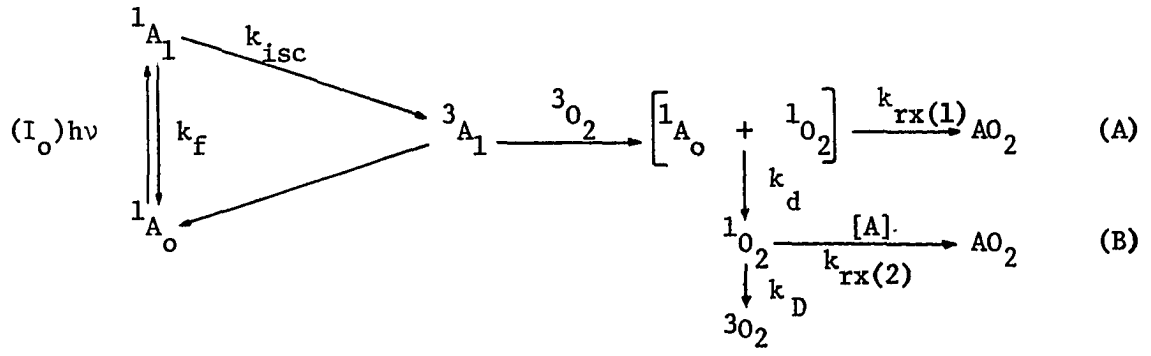
$$-\frac{dA}{dt} = k_{^1O_2}\frac{k_{rx}[A]}{k_{rx}[A] + k_D}$$

where $k_{^1O_2}$ represents the rate of formation of singlet oxygen. The above relationship is similar to that given on page 68, if expressed in terms of quantum yield of product formation, AO_2, and $\phi_{^1O_2}$. At low concentrations of substrate, 10^{-5} to 10^{-6} mole/liter, where k_d/k_{rx}, = β, is in the order of 10^{-2} - 10^{-3}, the equation reduces to:

$$-\frac{dA}{dt} = k_{^1O_2}\frac{k_{rx}[A]}{k_D}$$

which is the first order kinetics.

2. Direct Photooxidation:



At high concentrations of A, the major photooxidation products, >98%, occur via path (B). However, at low concentrations, 10^{-5}, path (A) is favored. One interesting aspect of path (A) is the possibility that this reaction could differ from the singlet oxygen reaction.

The rate disappearance of A at low concentration is expressed by the following equation:

$$-\frac{dA}{dt} = I_o \varepsilon [A] \ (1-^{\phi}F) \ \frac{k_{rx(1)}}{kd}$$

where ε is the extinction coeffient and $^{\phi}F$ is the quantum yield of fluorescence.

Zwicher and Grossweiner [51] studied the photosentized oxidation of aqueous phenol by eosin. The elementary processes and their corresponding rate constats are tabulated in Table XIV, where D is the ground state of aqueous eosin, $^1D^*$ is the lowest excited singlet state and ^3D is the lowest triplet state. Their works primarily emphasized the studies of the photoexcitation of eosin, the nature of triplet eosin, the reaction of triplet eosin and free radical reactions.

Kasche and Lindqvist conducted the kinetic analyses of the primary reaction between triplet fluorescein and molecular oxygen in aqueous solutions over a wide range of pH [20] based on the following reaction sequences.

$$T \longrightarrow S \qquad k_1 \qquad (1)$$

$$T + T \longrightarrow S + T \qquad k_2 \qquad (2)$$

$$T + S \longrightarrow S + S \qquad k_3 \qquad (3)$$

$$T + T \longrightarrow X + R \qquad k_4 \qquad (4)$$

$$T + S \longrightarrow X + R \qquad k_5 \qquad (5)$$

T,S,R and X represent the triplet, ground state, semireduced and semioxidized dye, respectively.

TABLE XV

ELEMENTARY REACTIONS OF THE EOSIN-PHOTOSENSITIZED OXIDATION OF PHENOL IN AQUEOUS SOLUTION[51]

	$D + h\nu \longrightarrow {}^1D$	
(1)	${}^1D \longrightarrow D + h\nu$	$k_1 = 1.3\times10^{-8}$ sec.$^{-1}$
(2)	${}^1D \longrightarrow D$ + heat	$k_1 = 4.4\times10^{8}$ sec^{-1}
(3)	${}^3D \longrightarrow D$ + light + heat	$k_3 = 420$ sec^{-1}
(3)	${}^3D + {}^3D \longrightarrow 2D$	$2k_3 = 2.4\times10^{9}$ M^{-1} sec^{-1}
(4)	${}^1D + C_6H_5OH \longrightarrow D + C_6H_5OH$	$k_4 = 1.4\times10^{10}$ sec^{-1}
(5)	${}^3D + O_2 \longrightarrow D + O_2$	$k_5 = 1.6\times10^{6}$ M^{-1} sec^{-1}
(6)	${}^3D + O_2 \longrightarrow$ Products	$k_6 = 9.1\times10^{3}$ M^{-1} sec^{-1}
(7)	${}^3D + C_6H_5OH \longrightarrow DH\cdot + C_6H_5O\cdot$	$k_7 = 1.5\times10^{5}$ M^{-1} sec^{-1}
(8)	$DH\cdot + C_6H_5O\cdot \longrightarrow D + C_6H_5OH$	$k_8 = 6\times10^{9}$ M^{-1} sec^{-1}
(9)	$D^{\cdot-} + C_6H_5O\cdot \longrightarrow D + C_6H_5OH + H^+$	$k_9 = 3.5\times10^{9}$ M^{-1} sec^{-1}
(10)	$DH\cdot + DH\cdot \longrightarrow D + DH_2$	$2k_{10}k_{11} = 1.4\times10^{16}$
(11)	$C_6H_5O\cdot + C_6H_5O\cdot \longrightarrow$ Products	
(12)	$C_6H_5O\cdot + H\cdot \longrightarrow C_6H_5OH$	$2k_{11} + k_{12} = 6\times10^{9}$ M^{-1} sec^{-1}

The results of the study of reactions between the triplet dye and molecular oxygen also indicate evidence for the occurrence of a "physical quenching" reaction,

$$T + O_2 \longrightarrow S + O_2 \qquad k_6 \qquad (6)$$

and a chemical quenching reaction.

$$T + O_2 \longrightarrow X + HO_2(\text{or } O_2^-) \qquad k_7 \qquad (7)$$

They concluded that the rate of triplet decay after flash exposure can be expressed by the equation:

$$-\frac{d\ln C_T}{dt} = k_1 + (k_2 + 2k_4)C + (k_6 + k_7)C_{O_2}$$

where C and C_{O_2} are the concentration of fluorescein and oxygen, respectively.

Termination Reactions

In the termination step of the photooxygenation reaction, singlet oxygen or other oxidizing species react with a suitable substrate to produce oxygenation products which may be stable or unstable. In the latter case, termination reactions such as rearrangement, decomposition or reactions with solvents can occur which may result in the complication of the reaction mechanism [14].

It is beyond the scope of this work to review all the termination reactions involved in photooxygenation processes. The following literature review will be restricted to the fate of peroxides or hydroperoxide, which with high probability, are the intermediates in the direct or indirect photooxidation of the organic compounds of interest.

There are different ways that peroxides or hydroperoxides can

decompose. Three of these mechanisms are presented here [12,39].

1. Unimolecular homolytic scission of O-O bond.

$$R\text{-}O\text{-}O\text{-}R \longrightarrow 2RO\cdot$$

The radicals produced by dissociation can either decompose further by β-scisson, or attack other molecules in the system resulting in the formation of new radicals. The activation energies for the series of ethyl peroxide through t-butyl peroxide are 34 to 37 Kcal/mole. Decomposition products for ethyl peroxide are ethanol and acetaldehyde, resulting from the disproportionation between ethoxy radicals:

$$2CH_3CH_2O\cdot \longrightarrow CH_3\text{-}CH_2\text{-}OH + CH_3CHO$$

They could also result from a chain process in which an ethoxy radical extracts hydrogen from a peroxide molecule and is subsequently decomposed by β-scission.

$$CH_3CH_2OOCH_2CH_3 + CH_3CH_2O\cdot \longrightarrow CH_3\dot{C}HOOCH_2CH_3 + CH_3CH_2OH$$

$$CH_3\dot{C}HOOCH_2CH_3 \xrightarrow{\beta\text{-scission}} CH_3CHO + CH_3CH_2O\cdot$$

2. Induced decomposition is a bimolecular process of radicals combining with a peroxide causing its decomposition. The attacking radicals can be produced directly from the peroxide itself or by subsequent reactions. The mechanism of the induced decomposition depends on the structure of the peroxide. It can be a hydrogen abstraction as in simple alkyl peroxide,

$$R\cdot + R'_2CH\text{-}O\text{-}O\text{-}CHR'_2 \longrightarrow RH + R'_2\dot{C}\text{-}O\text{-}O\text{-}CHR'_2$$

or an attack on O-O bonds as in benzoyl peroxide.

$$R\cdot + \phi\text{-}\underset{\underset{O}{|}}{C}\text{-}OO\text{-}\underset{\underset{O}{|}}{C}\text{-}\phi \longrightarrow \phi\text{-}CO_2^{\cdot} + R\text{-}O\text{-}C\text{-}\phi$$

The induced decomposition reaction consumes the initiator, R·, without increasing the number of radicals.

3. Decomposition by detonation is little understood and is not likely to occur at low peroxide concentration. Peroxides differ in their susceptibility to decomposition by detonation. In general, the lower the molecular weight the more susceptible is the peroxide to explosion. For example, of the alkyl peroxides, methyl peroxide is extremely dangerous, whereas t-butyl peroxide is unusually stable.

The above mentioned decomposition modes are the general thermal reactions and primary photodissociation will be reviewed in the following discussion. Primary photodecomposition of peroxides proceeds with the rupture of a weak R-O-O-R' bond [8], and in most cases is affected by the nature of the solvent and energy input, wavelength of light source.

$$ROOR' + h\nu \longrightarrow RO^{\ddagger} + R'O^{\ddagger}$$

$RO^{\ddagger}$ and $R'O^{\ddagger}$ are the intermediate excited radicals.

Relatively excessive energies are carried off by the separating radicals, i.e. 56 Kcal/mole at 3130 Å and 78 Kcal/mole at 2537 Å. Examples of the decomposition reaction of some alkyl peroxides are given below:

1. Dimethyl peroxide will undergo photodissociation at 2537 Å and may be followed by complete fragmentation of $CH_3O^{\ddagger}$.

$$CH_3OOCH_3 + h\nu \longrightarrow CH_3O^{\ddagger} \text{ (or } CH_2O + H) + CH_3O^{\ddagger}$$

2. In the UV region, the following reaction is postulated for diethylperoxide:

$$C_2H_5OOC_2H_5 + h\nu \longrightarrow C_2H_5O^{\ddagger} \text{ (or } CH_2O + CH_3) + C_2H_5$$

3. At 3200 Å, t-butyl hydroperoxide decomposes following this reaction mode:

$$(CH_3)_3COOH + h\nu \longrightarrow (CH_3)_3CO^{\ddagger} + OH$$
$$CH_3COCH_3 + CH_3$$

Reactor Design Formulation

Cassano, et. al.[9] derived several mathematical relationships for different types of reactors. The derivation of equations is based on a simple reaction system obeying the following conditions:

1. Isothermal.
2. Constant physical properties.
3. Monochromatic light.
4. No dark reactions.
5. Rate is first order with respect to light absorption by one of the reactants, and first order with respect to the concentration of the same reactant.
6. Flat concentration and velocity profiles.
7. Negligible reflection of radiation.
8. Steady state flow.

Three types of reactors of interest are: the parallel plate, cylindrical reactor and annular reactor.

Parallel Plate Reactor

This exists when light rays are uniform (Figure 7) parallel and

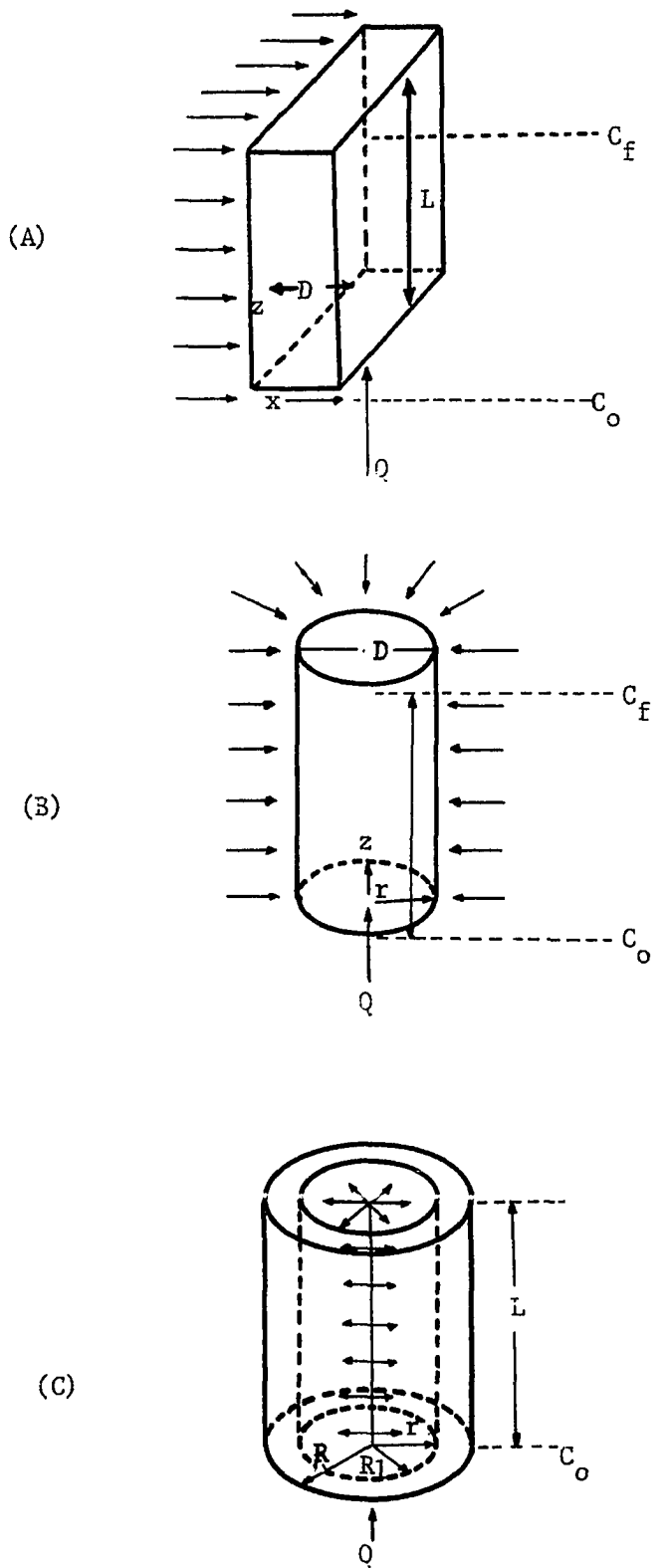


Figure 7. Reactor Geometries [9].

perpendicular to the wall of the reactor. The wall consists of parallel plates with a light path, D, and a flow length, L. The rate of production is:

$$\Omega = kI_a C \tag{1}$$

Radiation equation is given by:

$$dI/dx = -\mu I = -\alpha CI \tag{2}$$

With boundary conditions applied:

$$x = 0, \; I = I_w \tag{3}$$

For constant transport properties, monochromatic light and incompressibility flow, the mass balance is generally expressed as:

$$-\nabla C_i + (D_i + D_l^{(t)}) \nabla^2 C_i + \Omega_i = \partial C_i/\partial t \tag{4}$$

where Ω_i is the local rate of production of species i.

The mass balance equation for the parallel plate reactor reduces to:

$$\bar{v} \frac{dC}{dz} = \bar{\Omega} \tag{5}$$

where the bar designates average values across the light path of thickness, D. The boundary conditions are:

$$z = 0, \; C = C_o \tag{6}$$

Substituting $I_a = \mu I = \alpha CI$ into Equation (1), then:

$$\Omega = kI\alpha C^2 \tag{7}$$

Integrating Equation (2) and (3) to give I at any x, and substituting the result for I in Equation (7), gives:

$$\bar{\Omega} = \frac{kI_w C}{D} [1-\exp(-\alpha CD] \tag{8}$$

Solution of Equation (5) and (6) yields:

$$\frac{V_R k I_w}{QD} = \int_{C_t}^{C_o} [1-\exp(-\alpha CD)]^{-1} \frac{1}{C} \, dC \tag{9}$$

The dimensionless group on the left is a measure of V_R/D, the volume required per unit of light path. It is a function of conversion x,

$$x = 1 - C/C_o = 1 - \Gamma \tag{10}$$

Equation (9) can then be expressed in terms of Γ:

$$\frac{V_R k I_w}{QD} = \int_{\Gamma}^{1} [1-\exp(-\alpha C_o D)]^{-1} \frac{d\Gamma}{\Gamma} \tag{11}$$

Cylindrical Reactor

The lamp is outside the reactor and provides uniform, parallel and radical radiation. It is known that for unidirectional, monochromatic radiation, the radiation equation is given by:

$$\nabla \cdot I = -\mu |I| \tag{12}$$

where the product $\mu|I|$ is the volumetric absorption rate I_a. For cylindrical reactor, Equation (12) is reduced to:

$$\frac{I}{r}\frac{d}{dr}(eI) = \pm \mu I \tag{13}$$

with boundary conditions.

$$r = R, \; I = I_w \tag{14}$$

Replacing μ with αC and integrating it gives:

$$I = \frac{I_w R}{r} \{\exp [-\alpha C(R-r)] + \exp [-\alpha C(R+r)]\} \tag{15}$$

Proceeding with the parallel plate reactor leads to the final result:

$$\frac{V_R k I_w}{QD} = \tfrac{1}{4} \int_{\Gamma}^{1} [1-\exp(-\alpha C_o D]^{-1} \frac{d\Gamma}{\Gamma} \tag{16}$$

Annular Reactor

In this type of reactor, the radiation comes from a cylindrical lamp inside the annulus in a uniform, parallel and radial beams (Figure 7c). If the intensity is I_w and the ratio of outer to inner radius of the

annulus is $\gamma = R_2/R_1$, the final result is:

$$\frac{V_R k I_w}{QD} = \frac{1+\gamma}{2} \int_{\Gamma}^{1} [1-\exp(-\alpha C_o D)]^{-1} \frac{d\Gamma}{\Gamma} \qquad (17)$$

The notations used in the above discussion are:

C = concentration, gram-mole/cc.

D = length of light, cm.

I = light intensity, einstein/sec.cm^2.

I_a = volumetric rate of light absorption, einstein/sec.cm^2.

k = kinetic constant.

L = length, cm.

Q = volumetric flow rate, cc/sec.

R = radius, cm.

r = radial distance, cm.

V_R = reator volume, cc.

v = velocity, cm/sec.

x = length, cm. conversion or mole fraction.

z = axial distance.

α = molal absorptivity, cm^2/gram-mole.

Ω = local rate of reaction, production, gram-mole/cc.sec.

μ = attenuation coefficient.

subscripts:

f = exit or final condition.

w = reactor wall.

x = x direction.

z = z direction, axial.

- = average.

o = initial or inlet condition.

Application of Photochemical Processes in Wastewater Treatment

Photochemical reactions relating more specifically to the pollution abatement field have been reported by several agricultural chemists. Mitchel [7] noticed that under ultraviolet exposure, pesticide compounds can undergo structural changes. The bleaching phenomena indicates the possibility of color removal by radiation process. The use of UV rays for the disinfection of a public water supply was reported by Luckiesh.

Bulla and Edgerly [7] studied the photochemical degradation of some chlorinated hydrocarbons: aldrin, dieldrin and endrin. Using the General Electric G15TS Germicidal Mercury Vapor Lamp that provides an ultraviolet emission of approximately 2.9 w, 0.69 cal/sec, over a very broad wavelength band centered at 2537 Å, they studied the effect of time, power input and depth of the solution. The results of their investigations can be summarized as follows:

$$\text{Time:} \quad C/C_o = e^{-k(\text{Time})}$$

$$\text{Power:} \quad C/C_o = e^{-j(\text{Power})}$$

$$\text{Depth:} \quad C/C_o = a\,(\text{Depth})^b$$

where:

k,j,a and b are constants that can be determined experimentally;

C_o and C are concentrations at time = 0; and

time = t, respectively.

Combining the three parameters, the general equation is given by:

$$\text{Fraction degraded} = 1 - C/C_o = m(\text{Depth})^n \cdot (1 - e^{-y(\text{Time}) - (\text{Power})})$$

where m, n and y are constants.

The bioassay study of the irradiated aldrin solution showed a

significant reduction in toxicity to bluegills. The cost estimation for 50% degradation of pesticides at 10 cm. depth is given in Table XVI.

TABLE XVI

COST ESTIMATION FOR 50% DEGRADATION OF PESTICIDES AT 10 CM DEPTH

Compound	Cost/million gallons $
Aldrin	24.50
Dieldrin	73.00
Endrin	57.00

Note: based on power consumption at $0.015/Kw. hr. [7].

A study was made by Meiner, et. al. [32] of the effects of ultraviolet radiation on the rate and extent of chlorine oxidation of organic materials in a highly nitrified effluent from biological sewage treatment plants. They concluded that the extent of oxidation, which can be achieved by chlorine combined with UV radiation, is usually much greater than that which can be achieved by chlorine alone.

The rate of catalytic oxidation is dependent on pH, and a pH of 5 was found to be the optimum as far as the rate was concerned. In seven different experiments performed at pH 5, the average COD decrease was 67% in 5 minutes, 79% in 10 minutes and 95% in 15 minutes.

The rate of organic oxidation is not proportional to the chlorine concentration. A large excess of chlorine did not enhance the reaction rate, but simply increased the amount of chlorine required to reduce a given amount of organic matter.

Temperature has no significant effect on the rate and extent of catalytic oxidation at pH 5. A substantial reduction in both the rate and extent by the presence of ammonia was observed. UV-catalyzed chlorine oxidation indicated that phenol, 2,4 dinitrophenol, glycine, formic acid and O-dinitro benzene are oxidized rapidly and extensively. Process costs of 7.2¢ and 11.1¢ per 1000 gallons were estimated based on several types of commercially available lamps.

Kinney and Ivanuski [23] conducted research work on the photocatalytic oxidation of dissolved organic matter by irradiating slurries of zinc-titanate ($ZnTiO_2$), zinc-oxide, titanium dioxide and beach sand by sunlamps. The conclusions drawn from their works are:

1. That the reaction appears to follow first order kinetics.
2. ZnO appears to be superior for the light induced oxidation.
3. At a concentration of 100 to 200 mg/l of organic carbon; 80% of phenol, 67% benzoic acid, 44% acetic acid, 40% sodium stearate and 16% sucrose were oxidized in 24 hours with 10 g/l zinc-oxide.
4. Rose Bengal and Sudan Orange are ineffective sensitizers.
5. Beach sand showed some photosensitization properties when illuminated, eighty seven percent phenol was removed in 72 hours. This strongly suggests that photocatalysts are widely distributed in nature and that photosensitized oxidation is a mechanism whereby dissolved organic matter is oxidized in the natural environment of streams and lakes.
6. Dissolved organic matter in a sample of domestic sewage

was reduced, 50% in 24 hrs. and 75% in 70 hrs.

7. The limiting factor appears to be the activity of the sensitizer, since light intensity dropped substanially without measurable decrease in reaction rate.
8. The application of photosensitized oxidation is more feasible in systems with high concentrations of organic matter since the amount removed at constant irradiation increases with increased concentration.

This last conclusion may be true under particular reaction conditions. In the subsequent chapter the experimental evidence will indicate that a deviation from this is possible.

Smith [49] has been investigating the prospect of a photochemical process as means of tertiary water treatment. Preliminary results indicate that a reduction in COD of 25-50% can be achieved without a sensitizer. When Fe ion was added as a sensitizer, the reduction was not substantially greater.

The work of Miller and Narang [33], although not directed toward the photochemical reaction in water pollution abatement, may lead to a feasible process for the removal of pesticides. They discovered that photolysis of certain alkyl halides and aromatic amines produces dehalogenation of halides. These reactions involved a photoinduced charge transfer from the amine to the halide. Photolysis of DDT and diethylamine at 3100 Å yields 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene (DDC), 1,1-dichloro-2,2-bis(p-chlorophenyl) ethane (DDD), p,p'-dichlorobenzophenone (DDCO) and HCL. Photolysis of DDT does not occur unless an inducer which has a low ionization potential such as diethylaniline, is present.

The results of their studies are summarized in Table XVII.

TABLE XVII

EFFICIENCY OF INDUCED PHOTOLYSIS OF DDT[33]

Inducer ($M \times 10^{-3}$)	HCl Formed (moles $\times 10^{5}$)	DDT Consumed (moles $\times 10^{5}$)
None	0	0
Triphenylamine	1.3	6.5
N,N-Diethylaniline		8.7
Benzophenone	0	0
Quinoline	0	0
Diphenyl Sulfide	1.5	2
p-Nitrotoluene		0
p-Phenylenediamine	20	6.5
1-Aminoanthraquinone	0	0
Benzidine	6.6	5.6

Note: Determined by irradiation of 100 mg. of 98% p,p'-DDT in 50 ml of cyclohexane for 5 hrs.

Prather [38] studied the autoxidation of refinery waste and he assumed that the chain reactions as described on p.19 were applicable to process. Using an aeration tower, 25' x 4' x 6', Prather succeeded in removing over 50% of applied COD. Residence time for water flowing through the tower was estimated at 3 to 6 minutes, and air flow through the tower averaged 7600 cfm. He postulated that light would enhance the reaction rate.

Bishop, et. al [4] conducted research on catalytic hydrogen peroxide oxidation of refractory organic material in secondary municipal waste treatment plant effluents, in concentrated municipal effluents from a distillation process, in collapsed foamate from foaming studies and in very dilute municipal effluent from carbon absorption treatment. ACS reagent grade ferric sulfate, ferric ammonium sulfate and ferrous ammonium sulfate were used as catalysts. The reaction mechanisms believed to be responsible for the process were:

$$Fe^{++} + H_2O_2 \xrightarrow{k_1} Fe^{++} + OH^- + \cdot OH$$

$$Fe^{+++} + H_2O_2 \xrightarrow{k_2} Fe^{+++} + \cdot HO_2 + H^+$$

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + OH^-$$

$$HO_2\cdot \longrightarrow O_2^- + H^+$$

$$Fe^{+++} + O_2^- \longrightarrow Fe^{++} + O_2$$

$$H_2O_2 + \cdot OH \longrightarrow HO_2\cdot + H_2O$$

$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$

$$R + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

$$ROOH + Fe^{++} \longrightarrow RO\cdot + Fe^{+++} + OH^-$$

$$ROOH + Fe^{+++} \longrightarrow RO_2\cdot + Fe^{++} + H^+$$

They concluded that:

1. The ferric-ferrous ion hydrogen peroxide catalytic systems oxidized an appreciable portion, 70%, of the refractory organic material.
2. The process involved free radical oxidation, ·OH, and autoxidation at an optimum pH of 3-5.

3. The Fe^{+++} catalyst required an elevated temperature, $65^{o}C$, to produce practical oxidation rates. The ferrous system, on the other hand, produced rapid oxidation at ambient temperatures.
4. Thirty-six to sixty-five percent of COD was oxidized to carbon dioxide and water, but an oxidation resistant residual remained.
5. In the ferric-peroxide system, stoichiometric ratios of an oxidant to wastewater COD produced an oxidation efficiency of approximately 60% for a 22-hour reaction time. In the ferrous system, the oxidation efficiences were 15 to 50% lower than the former, but required only a 20-minute reaction time.
6. Because of the high cost of hydrogen peroxide and the limited pH range, 3-5, of the oxidant, the ferric-ferrous ion hydrogen peroxide catalytic systems were not practical as a source of oxidants for use in wastewater treatment.

CHAPTER III

MATERIALS AND METHODOLOGY

Introduction

The literature cited in the previous chapter indicates that direct or indirect photochemical oxygenation has been studied by several investigators; however, the application in water pollution abatement that has been published is primarily the works of Bulla & Edgerly [7], Kinney & Ivanuski [23] and Smith [49]. The photochemists working with pure compounds, generally non-aqueous solutions and high concentrations, are primarily interested in the mechanisms and the preparations of photooxygenated products. In contrast, sanitary engineers dealing with dilute aqueous systems are mainly concerned about the extent of the reactions, i.e. the reduction of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD).

As stated in the objective of this research work, the study will be directed specifically toward acquiring knowledge pertinent to process characteristics of photooxygenation in aqueous systems. One of the most important reaction parameters is the rate at which the substrate is transformed or oxygenated into its corresponding reaction product(s), and the rate of complete destruction of the organic compound being irradiated. Within such experimental framework, the investigations were performed in three stages:

1. Preliminary experiments with the objective being to study the

susceptibility of some organic compounds to photodegradation, direct photooxidation and indirect (sensitized) photooxidation and to determine the reactivity of dye and pigment sensitizers.

2. Subsequent experiments from the results obtained. Five or six compounds, having particular structures, aromatic, straight chain or cyclic, are further investigated to determine their rates of reaction, susceptibility to photodegradation, reactivity to oxygen and the extent of the reaction in terms of COD and BOD reduction.
3. Final experiments to study the applicability of photooxidation to some industrial wastes, i.e. aqueous solution containing vegetable oil, paper pulp and cyanide.

Selection of Organic Materials

There are numerous organic compounds known to be resistant to biochemical oxidation. Nevertheless, as discussed earlier in Chapter I, there is no generalized pattern that can be used to predict the susceptibility of organic compounds to biodegradation. The studies made to date are primarily related to the basic concepts of dissimilation [40], nonbiodegradability [18] or tabulation of the relative resistance degree of organic compounds to biochemical oxidation [46].

To study the extent of photodegradation or photooxidation of organic materials in aqueous solutions, the selection of the compounds cannot be based solely on their recalcitrance to biooxidation. Other factors to be considered are their solubilities in water, their method of detection, and

unique chemical structures: aliphatic, aromatic or cyclic. Based on these requirements the following compounds were selected for the studies.

Methanol, Formic Acid, Ethanol, Acetic Acid, Propanol, Propionic Acid and Butanol

It is postulated that the intermediate in the photodegradation or photooxidation will be the C_1, C_2 or C_3 fragments. The fate of these low carbon fragments when exposed to photons under the presence or absence of oxygen will determine the extent of the photochemical reaction. If these compounds are readily oxidized or dissociated into CO or CO_2, then the reduction of COD or BOD of the corresponding solution would be substantial. On the other hand should these chemicals show a high resistance to photooxidation or if the oxygenated products are not CO or CO_2 and remain in solution, then it can be concluded that the removal of oxidizable organics from aqueous solutions, measured in terms of COD, by photochemical reaction is not effective.

Iso-Butyl Alcohol, t-amyl Alcohol

It is known that the branching of straight chain aliphatic compounds can make it more amenable to photodegradation than its corresponding straight chain homologs.

Hexyl Alcohol

Hexanol is quite readily biooxidized; however, the study on the reactivity and degradability of this alcohol may reveal some information that could be extrapolated to long chain aliphatic compounds. The selection is also based on the fact that hexanol is the last of the homologs that is fairly soluble in water.

Phenols

Phenol and its derivatives are generally toxic to the wastewaters

organisms. However, if acclimatized, the organisms will be able to use these compounds for their carbon source. Considering the high energy bond in the benzene ring and the problems that phenol or its derivatives may create in the environment, it is worthwhile to explore how photodegradation or photooxidation can break this compound into smaller less toxic fragments.

Toluene

Under general conditions, toluene is biodegraded very slowly, but benzoic acid which is the oxidation product is more amenable to biochemical oxidation than its parent compound [46].

Hexyl Amine

Malney and Gerhold [30] studied the ability of activated sludge from municipal waste treatment plants to oxidize various aliphatic compounds. The experimental results indicate that all amines, including hexyl amine, are toxic to sludge organisms. Photochemically, aliphatic amines will undergo photodissociation into RNH radical and hydrogen, or a breakdown of C-N bond. The absorption peak of the amine mostly lies below 2500 Å. Based on this consideration, it is interesting to study the susceptibility of hexyl amine to photochemical reactions.

Sodium Stearate

Stearic acid is insoluble in water but its sodium salt is fairly soluble. The breakdown study of this derivative may give some information as to the extent vegetable oil, in which stearic acid is commonly found, can undergo photooxidation.

Dodecyl Sodium-Sulfate

Dodecane, a C_{12} straight chain hydrocarbon, which may be one of the constituents in a refinery waste, is insoluble in water. It was found that

even at low concentrations, less than 500 ppm, the stripping of dodecane by oxygen/air was much faster than the rate of the photochemical reaction. Also, the sodium salt of the sulfonated dodecane dissolves in water and hence, it can be used for the experiment. It is realized that the sulfonated derivative may have entirely different susceptibility to photochemical reactions. In spite of this, it is interesting to observe how a C_{12} straight chain aliphatic compound undergoes photooxidation.

Cellulose

Certain organisms can use cellulose for their carbon source, but this compound is generally biodegraded very slowly. The fragmentation of this chain high molecular weight organic could result in reducing its resistance to biochemical oxidation.

Vegetable Oil

Edible oil, grease and fats frequently cause problems in domestic waste treatment systems. If an unconventional effective method could be developed, it will undoubtedly be very helpful in improving the performance of the treatment plant.

Cyanide

This toxic anionic compound is usually eliminated by oxidation-reduction processes using chlorine gas under high alkaline conditions. This treatment method is considered to be the most practical and economical; however, at least a 24-hour reaction time is required for complete oxidation. It is postulated that singlet oxygen will react with a singlet state cyanide and oxidize this obnoxious inorganic ion into nitrogen and carbon dioxide.

Selection of Sensitizers

As discussed in Chapter II, the sensitizers of interest in photooxidation are those that show high reactivity to oxygen. Based on the classification suggested by Bourdon and Schnuriger, and the experimental results of other investigators [14,17,43], the following sensitizers were used in the preliminary experiments:

Acridine Orange	(Acridine Dye)
Eosin Yellow	(Xanthene Dye)
Rhodamine B	
Methylene Blue	
Rose Bengal	
Crystal Violet	

Pigment sensitizers that are known to have a substantial reactivity to oxygen are the oxides of zinc, titanium and the sulfide of zinc [16,11, 23,31]. In spite of the previous work in pigment sensitization, it is considered worthwhile to make comparison studies of this process with the other oxidation reactions, direct and dye sensitized oxidation. On the basis of this consideration, the inorganic sensitizers chosen were:

ZnO
ZnS
$ZnCO_3$
TiO_2

To study the photosensitized oxidation "at a distance", silica gel and ion exchange resins were used as inert solid particles on which the dye molecules were attached. Cation exchange resins, Dowex-50x, 20-50 mesh and 50-100 mesh, can be used to bind acridine orange and methylene blue as these dyes are cationic in nature. Anionic eosin yellow can be attached

to an anionic exchange resin, Dowex 1X, 20-50 mesh and 50-100 mesh.

Photochemical Reactor

There are various reactors available, but the one considered to be the most practical for this experimental work for sampling is the 1000 ml. Ace Glass Model 6523, water jacketed reaction vessel with stopcock. For the studies of photodegradation and direct photooxidation, a quartz immersion well (Ace Glass Model 6515-B-27) was used and borosilicate immersion well (Ace Glass Model 6517-E-10) was selected for the photosensitized reaction experiments. These immersion wells are double-walled with inlet and outlet tubes for cooling water.

The photochemical immersion lamps considered to be appropriate are the Hanovia high pressure 550- and 450-watt quartz mercury vapor lamps having a spectral energy distribution as presented in Table A-1, Appendix A. To restrict portions of the radiated energy from reaching the reactant material, and to study which portion of the spectrum creates the reaction, three different absorption sleeves were used. These included Ace Glass Vycor 7010-40, Corex 9700-42 and Kimax KG-33-44.

For the above photochemical lamps, a reactive type transformer which can supply the extra voltage and current required to initiate the arc was used. It is an open "core and coil" type, Ace Glass Model 6515-36-D-62.

Analytical Techniques

An F-M Gas Chromatograph Model 810 with flame detector was used for determining the change in concentration of the irradiated chemicals. Gas chromatography is known for its versatility, speed, simplicity and low cost. In recent years it has become one of the most useful and popular analytical

tools. The applications have reached into all branches of chemistry despite its limitations, which are:

1. The sample must have an appreciable vapor pressure at the column temperature.
2. The chromatograph provides only a limited amount of data --retention time, peak size and peak shape.
3. And must comprise among speed, resolution and capcity; it is impossible to optimize all three at the same time.

Based on the understanding of the nature and limitations of the gas chromatography and considering the objective of the research work, the use of this analytical tool for measurements of the conversion of the irradiated solution was deemed appropriate.

The selection of the suitable detector is another factor that is highly important as this can determine the reproducibility of the data obtained. A flame ionization detector is characterized for its insensitivity to water, permanent gas, Co, CO_2 and most inorganic compounds; therefore, it is advantageous and convenient for the analysis of aqueous solutions. On the other hand, the response of a flame detector depends upon "the number of molecules per unit of time" that enter the detector and is not dependent on the concentration of these molecules in the carrier gas. This is the opposite of thermal conductivity detectors, which are sensitive to concentration and respond accordingly. In spite of this response, a flame detector can still be used for measuring relative change of chemical concentrations in solutions, provided the operation conditions are kept constant. The reproducibility is very much affected by the method in which the sample is injected. Because of this, the injection of the

samples should be carried out carefully and in a proper manner throughout the analyses.

Standard columns as recommended in the literature [27,41] were used. These are: Carbowax 20-M for alcohols, ketones and amines; and Apiezon L for phenols. Newly packed columns containing different packing materials, such Porapak Q, AS and P were tried but they were inferior and less efficient than the previous mentioned materials. Isothermal conditions were applied with the oven temperature set at the boiling point of the chemical being injected into the chromatograph.

Helium was used as a carrier gas at a flow rate of approximately 100 ml/min. It was found experimentally that the corresponding optimum flow rates for hydrogen and air were 55 ml/min. and 375 ml/min., respectively.

COD tests as described in Standard Methods [41] were conducted for the determination of the remaining oxidizable organics. BOD tests were also run, using for seed a settled effluent, 24 hrs., from an aeration unit which was fed articificial sewage having the composition as listed in Table B-1, Appendix B. It has to be pointed out that the use of artificial sewage that is not conditioned or acclimatized to the irradiated chemical may produce erroneous results. The errors involved may be due to the poisoning of the organisms by the irradiated chemical or to the failure of the organisms to use the chemical for their carbon source. Although conditioning is desirable, it is not practical because the composition of the irradiated waste is unknown. Taking into consideration that the BOD tests were intended to measure the relative change in biodegradability of the original and the irradiated solutions, the use of unconditioned sludge for seed was more realistic than the application of acclimitized organisms.

Cyanide concentrations were determined by using titrimetric and colorimetric procedures as described in Standard Methods [41].

Experimental Procedures

In the preliminary experiments the following organic compounds and sensitizers were irradiated:

Organic Compounds	Sensitizers
Phenol	Acridine Orange
t-amyl Alcohol	Eosin Yellow
Hexyl-Amine	Methylene Blue
Dodecane	Crystal Violet
Xylene	Rhodamine B
Toluene	Rose Bengal
Benzene	Zinc Oxide
Hexanol	

One thousand milliliters of solutions, with concentrations ranging from 100 to 1000 mg/l, were exposed to UV irradiation for 2-4 hours. The selection of the reaction time is arbitrary, as the main purpose of these experiments is to observe the relative reactivity of the compounds, or sensitizers, to photochemical reactions. Three parameters considered to be the controlling ones are:

1. Substrate concentration;
2. Sensitizer concentration or sensitizer to substrate ratio;
3. And, light source or effective spectra.

On the basis of this understanding, the above mentioned chemicals were tested for susceptibility toward photodegradation, direct photooxidation and photosensitized oxidation. For the first two processes, a quartz immersion well that allowed at least 50% of the UV region to pass through was used, while a borosilicate immersion well was used for the photosentized

reaction. Although it is conceivable that shorter wavelengths can enhance the sensitization reaction, the study of the effectiveness of the visible spectra to photosensitized oxygenation if successful, can produce meaningful and applicable information.

From earlier discussions in Chapter II, it is known that the formation of molecular singlet oxygen is by way of energy transfer from the excited triplet sensitizer to the ground state oxygen. Considering the energy levels of the excited molecular singlet oxygen, 22 Kcal and 37 Kcal above ground state, light of the visible region will have sufficient energy for the formation of the triplet state sensitizer and will subsequently transfer its energy to ground state oxygen and form the excited state. In addition to this energy consideration, the application of the visible spectra will be more feasible in practice than in the use of short wavelengths.

Due to the low solubility of oxygen in water, 8-9 mg/l at 20^{o}C, it was assumed that accurate control of the oxygen gas flow rate into the system was not critical. It was also assumed that the diffusion rate of gaseous oxygen into the aqueous solution is much faster than the rate of overall molecular singlet oxygen formation. By bubbling oxygen continuously, thus keeping the oxygen concentration in the solution constant throughout the process, it was assumed that there would be an excess of oxidant for complete oxidation to occur.

A constant flow of oxygen or air was maintained during the reaction and the flow was set at a rate such that it would not cause excessive loss or foaming in the reactor.

For the first few runs, 5 ml. samples were collected at 10-15 minute intervals. It was later changes to 60-minute intervals as the rate was

evidently slow. Five microliters of the solution were then injected into the Gas Chromatograph using a 10 microliter Honeywell Unimetric syringe. The change in peak height, which is proportional to the total area of chromatogram, was measured which indicated the relative concentration of the remaining organic compound in the solution.

It is necessary to point out that the reproducibility of the measurements by chromatographic technique was subjected to many factors; one of which was the method of injection. From experience and by repeating the measurement for each sample, the accuracy was held within a range of approximately 2.5%, while other conditions, i.e. gas flow rate, temperature, etc., remained constant.

From the results of the preliminary experiments, several chemicals were found to have unique molecular structures and four sensitizers were further explored.

Compounds	Sensitizers
Phenol	ZnO
Cyclohexanone	Eosin Yellow
Hexanol, Hexyl-Amine	Acridine Orange
Ethanol	Rose Bengal

Reaction time was 4 to 8 hours and BOD and COD tests were run for each sample. The selection of reaction time was again arbitrary, but it was considered necessary to extend it in order that additional information could be obtained.

For the study of sensitized oxidation, "at a distance" ion exchange resins were used as the inert materials on which the sensitizer molecules could be attached. Two hundred milliliters, wet, of a cationic exchange resin (Dowes 50X in Na-form) were exhausted by a concentrated solution of

Acridine Orange followed by rinsing with distilled water. The same procedure was applied to anion exchanger (Dower 1X) using a saturated solution of water soluble eosin yellow. Fifty and one hundred milliliters of the dyed resins were used to determine the effectiveness of the photosensitized oxidation "at a distance" of phenol and alcohol.

The following set of experiments were primarily intended to study the extent of photodegradation and photooxidation in terms of changing the COD of the irradiated solutions. Only sensitizers showing reactivity to this process would then be further investigated. To observe the chemical structure effect and chain length of the photon induced fragmentation process, the following chemicals were irradiated:

Methanol	Formic Acid
Ethanol	Acetic Acid
Propanol	Propionic Acid
Butanol	Iso-Butanol
t-amyl Alcohol	n-Hexanol
Na-Stearate	Dodecyl Sodium Sulfate
Phenol	Cyclohexanone

For these experiments 10 ml. samples were drawn at 30 or 60 minute intervals. COD and BOD tests were made to determine the residual oxygen demand. The concentration of the residual chemical was determined by using a gas chromatograph whenever possible.

The concluding experiments were designed to explore the application of known process conditions of some materials which are commonly found as main pollutants in industrial wastewaters. The materials being photolyzed were: vegetable oil, soybean oil which contains over 50% unsaturated fatty acids; paper pulp and free cyanide, CN^-.

Emulsions containing 2.5-5 ml. of oil per liter were directly photo-oxidized for a period of eight hours. To measure the extent of the reaction, BOD and COD tests were run on samples collected at 60 minute intervals.

Suspension of approximately 150 mg/l of paper pulp, prepared from toiled paper, was photooxidized and photosensitized, using ZnO. The same analytical procedures were utilized as in the preliminary experiments.

Cyanide solution containing 125-100,000 mg/l free CN^- was photooxidized directly at a pH above 12. The effect of ZnO was also studied. The remaining CN^- in solution was measured by titration and colorimetric methods as described in Standard Methods [44].

As a final experiment, light induced chlorination, using sodium hypochlorite solution, was explored for its effectiveness in the destruction of free cyanide in aqueous solution. This experiment is illustrated in Figure C-1 of Appendix C.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Preliminary Experiments

As described in the previous chapter, the objective of this experimental work is to study the relative effectiveness of photodegradation, photooxidation and photosensitized oxidation in aqueous systems. Knowledge of the physicochemical processes involved in an aqueous system is not fully established, hence, the experiments performed were oriented toward acquiring information pertinent to basic process characteristics.

One of these characteristics is the compound susceptibility to photochemical reactions. In Chapter II the impossibility of obtaining a quantitative theoretical prediction of the nature and efficiency of the possible primary process, which occur as the immediate result of light absorption --even for simple molecules is discussed. In aqueous systems the participation of solvent molecules or unknown factors compound the reaction problems. On the basis of these considerations, the susceptibility of an organic compound undergoing photochemical reaction in an aqueous system can only be evaluated experimentally.

The experiments produced and their results are found in Tables D-1 through D-18 of Appendix D. It should be noted that a negative result does not necessarily mean that the organic compound irradiated is resistant

to the photochemical reaction. The outcome of these experiments only indicates the relative reactivity of those compounds to photochemical processes under the applied reaction conditions, i.e. 30°C, 550 watt high-pressure lamp, 1000 ml. reactor, etc. It is a common belief that most organic compounds can be photochemically decomposed under appropriate reaction conditions.

A discussion of results can be summarized as follows:

1. Phenol has a maximum absorption peak at 2780 Å and below 2380 Å, consequently, the compound can only be degraded photochemically if irradiated by light in the UV region.
2. Direct photooxidation is more effective than photodecomposition as indicated by 60% conversion, compared to only 40% by the latter in the same reaction time. The solution becomes turbid and gradually turns dark brown, which may be attributed to the formation of humic acid compound(s), or colored product(s) from an oxidative coupling reaction.
3. Phenol could be photooxidized in the presence of ZnO and preliminary experiments showed that ZnO/substrate ratios control the extent of the reaction. Theoretically, the optimum ZnO/substrate ratio is 2:1. But as has been shown elsewhere, the formation of hydrogen peroxide, which is the oxidizing entity in the process, is affected by the concentration of organic compounds present in the system and tends to decrease when the concentration exceeds optimum concentration [11,31]. It is also true that the production of H_2O_2 increases with an increase of ZnO, but under

constant light intensity the blocking of the light may become the limiting factor.

4. The sensitized oxidation of phenol by dye sensitizers such as: Methylene Blue, Acridine Orange, Rose Bengal and Rhodamine B, is not as efficient as it was theoretically anticipated. These dyes are known to be reactive to oxygen and have triplet energy above 45 Kcal/mole, which is sufficient for the formation of singlet molecular oxygen, sigma or delta. The ineffectiveness of this process may be related to some of the basic reactions involved.

   a. the rate of formation of singlet molecular oxygen was very slow, or the physical/chemical deactivation of the formed singlet oxygen by other molecules, was much faster than its formation; hence, no net result was obtained.

   b. as discussed in Chapter II, the rate of formation of oxygenated products at high oxygen concentration is controlled by the formation rate of the sensitizer's triplet state. At low oxygen concentration, the quantum yield of product formation is [14,17]:

$$\phi_{AO_2} = {}^{\phi}{}^{3}S_1 \frac{[O_2]}{k_5/k_7 + [O_2]}$$

   For a substrate that is not overly reactive to oxygen the following equation applies,

$$\phi_{AO_2} = {}^{\phi}{}^{1}O_2 \left\{[A]/([A] + \beta)\right\}$$

   where β is defined as k_8/k_9. If k_8, i.e. the deactivation

rate constant of $^1O_2$, is high and $^{\phi}1O_2$ is low, then the quantum yield of product formation, AO_2, will also be low. This is also true for dye-sensitized oxidation of phenol.

5. Phenol can be photooxidized when Eosin Yellow is used as a sensitizer. This dye is more reactive than the other sensitizers used, but the conversion of phenol into its corresponding oxygenated product(s) is not strongly dependent on the concentration of the sensitizer as one would expect. The conversion remains approximately constant, 46-42%, when the sensitizer concentration is increased five fold --from 100 mg/l to 500 mg/l.
6. t-amyl alcohol is not degraded when irradiated under UV light. Since most alcohol has the first absorption band below 2000 Å [8], the failure of this photodegradation process is due primarily to the lack of energetic photons having sufficient energy to break the bonds.
7. Approximately 60% of t-amyl alcohol could be converted by direct photooxidation. This substantial transformation of the alcohol could not be expected on the basis of the reaction scheme outlined by Young [17] and other investigators [14,15] that required the presence of highly energetic photons, short wavelengths. An explanation will be presented later in this chapter.
8. The conversion of t-amyl alcohol by ZnO sensitization oxidation is less efficient compared to that of phenol.

9. No significant change of t-amyl alcohol is observed in the dye-sensitized reaction.
   a. related to the inefficiency of the production of molecular singlet oxygen (as discussed in 4a);
   b. that since the conversion was measured by gas chromatographic techniques, if the oxygenated product(s) has the same retention time as that of the alcohol, the overlapping of the peaks makes the estimation of the conversion erroneous.
10. About 60% of hexyl-amine is photooxidized in 2 1/2 hours, but on the other hand, photolysis in the absence of oxygen does not result in any significant change.
    Absorption of photons by a primary amine will result in the dissociation of the molecule into:

$$RNH_2 + h\nu \longrightarrow RNH + H$$

    In a condensed system the recombination of the radicals is very likely to occur; and hence, the net reaction result is negligible. Hexyl-amine is resistant to peroxide oxidation, ZnO sensitized photooxidation. However, the measurement of the residual amine in the irradiated solution indicates that the compound is susceptible to dye-sensitized oxidation.
11. The rate of transformation of hexyl alcohol into its oxygenated product(s) by direct photoxoidation is comparable to that obtained from the ZnO system. This slowness must be correlated to the lack of energetic photons or the

inefficiency of the triplet formation, which is the controlling reaction. A more detailed interpretation and discussion will be presented later.

The study of the photosensitized oxidation "at a distance", i.e. a heterogeneous system where the dye sensitizer molecules are attached on inert material, was discontinued because of the difficulty in finding suitable media. For this purpose, the inert material must meet the follow-requirements:

1. Its specific gravity must be slightly greater than that of water in order that the particles can be distributed uniformly in the suspension by simple mixing;
2. The material must strongly bind the sensitizer molecules so that they will not be leached off during the reaction.

Unsuccessfullness in obtaining a material having these properties and ineffectiveness of the dye sensitized photooxidation made it necessary to discontinue this study.

Subsequent Experiments

Having acquired some data on the effectiveness of the photochemical processes, i.e. photodegradation, photooxidation and photosensitized oxidation, the subsequent experiments were specifically directed toward obtaining more information concerning pertinent process characteristics.

It is speculated that physical or chemical reactions that can bring about structural change will affect, to a certain extent, the biodegradability of the compound. As discussed in Chapter I, the susceptibility of an organic compound to biochemical degradation depends strongly on various factors, e.g. selectivity of the organisms, environmental conditions, etc.

Hence, it is almost impossible to predict the nature of the reaction product with respect to its recalcitrance. In this study the problem has become more complicated as the chemical structure and the composition of the irradiated solutions are unknown. Therefore, the biodegradability of the compound(s) can only be determined experimentally by BOD test or other appropriate methods.

Another aspect of this process that concerns sanitary engineers is the removal efficiency of the oxidizable organics measured in terms of BOD and COD. It is not only the effectiveness or completeness in removing the undesirable organics from the solutions that is important, but also the rate at which this process takes place. The analysis of the experimental data leads to the generalized conclusions discussed in the following sections.

Effect of Photochemical Reaction on BOD/COD Ratios

In presenting the objectives of this research project it was anticipated that the changes in chemical structure, as the result of photolysis would make the compound(s) more amenable to biochemical reactions. This may be true for some compounds such as toluene, or it may be theoretically possible to find an optimum reaction condition for a compound such that the reaction product will show high response to bacterial growth.

The results of BOD and COD tests of the original and treated solutions indicate that of the sixty-one samples, within the accuracy of the test --±7.5%, thirty-eight did not show any significant change in BOD/COD ratios. Seventeen, 28%, showed reductions and six, or 10%, could be considered as having higher ratios. The results of these BOD/COD measurements are summarized in Table E-1 of Appendix E.

An attempt to find a generalization based on the data obtained was unsuccessful because of the inconsistency of the test results, which may be attributed to analytical errors or other unknown factors.

Constant BOD/COD ratio of the original solution and the irradiated solution cannot be interpreted as a true constant value of the correspond- BOD and COD. In the case of photolysis the results in the fragmentation of the compound into CO, CO_2 or other gaseous products, the BOD and COD will decrease proportionally and the ratio may remain constant. On the other hand, if the reaction product(s) remains in solution and is more amenable to biooxidation, dichromate oxidation, or if the reaction product exerts less BOD and COD than the original compound, the value of BOD/COD will not change significantly.

An increase in BOD/COD ratio does not necessarily lead to the conclusion that the irradiated solution is more susceptible to biodegradation than the corresponding original solution. If the product obtained from the irradiation process exerts the same BOD, but less COD than does the unexposed solution, an increase in BOD/COD ratio may be observed.

A similar fallacious interpretation is also possible for the decrease in BOD/COD ratio. Suppose the irradiated solution exerts the same BOD but higher COD than the original solution does, or the reaction product is very toxic to the organisms used as seed but it reacts readily with dichromate, then in both cases one would expect a decrease in BOD/COD ratio.

Although the evaluation of BOD/COD ratios of the photolyzed solutions sounds ambiguous and misleading, the tests lead to a tentative conclusion that pre-treatment of industrial wastes by a photochemical process will generally not enhance the biochemical process which may be used as a

subsequent treatment method.

The Extent of the Reaction

The extent of the reaction as understood in this study, is the effectiveness in removing the substrate or its reaction products from the solution in terms of COD remaining.

The discussion in Chapter II indicates that the kinetics of photooxidation reaction, direct or indirect, are well established. Therefore, a quantitative study on the reaction can be performed satisfactorily. However, this is beyond the scope of this research and from a sanitary engineering point of view, one is only concerned with the overall kinetics of the process with respect to organic removal. A sanitary engineer is inclined to apply the "black-box" approach whenever it is deemed practical.

On the basis of this understanding, the kinetic studies will be simplified because:

1. The reaction can be assumed to be psuedo first order with respect to the substrate photolyzed.
2. The overall reaction is unidirectional.
3. All the intermediates formed in the reaction steps are shortlived, relative to the reaction time applied.

In the previous work, the investigators shared a common belief that the reactions follow first order kinetics with respect to COD, or total organic carbon removal. Depending on reaction conditions, which will be discussed later, this assumption is true to a certain extent.

The plotting of the data is based primarily on the assumption that conversion of the compound into its corresponding products, or the removal

of the oxidizable organic, in terms of BOD and COD, is a pseudo first order reaction with respect to the compound irradiation. Using the simple relation given by:

$$-dC/dt = kC$$

or its integrated form,

$$\ln C_o/C_r = kt$$

or,

$$\log C_o/C_r = k/2.303t = k't$$

where:

C_o = initial concentration (mg/l substrate or its corresponding COD or BOD)

C_r = concentration remaining in the solution.

Plotting the values of C_o/C_r vs. time on semi-log paper will give a straight line with a slope equal to k' or k/2.303.

For a simple second order reaction, the integrated form of the rate equation is:

$$1/C_r - 1/C_o = kt$$

Therefore, plotting the values of $1/C_r$ vs. time will produce a straight line.

The plottings of the values of C_o/C_r vs. 30 or 60 minute reaction time intervals, show the following process characteristics:

Phenol

Figure 8 depicts that the photodegradation of phenol follows first order kinetics with respect to the substrate. However, after a 4 hour exposure, the reaction ceases as indicated by the constant, C_o/C_r (line 1 of Figure 8). It is very likely that after a substantial amount of

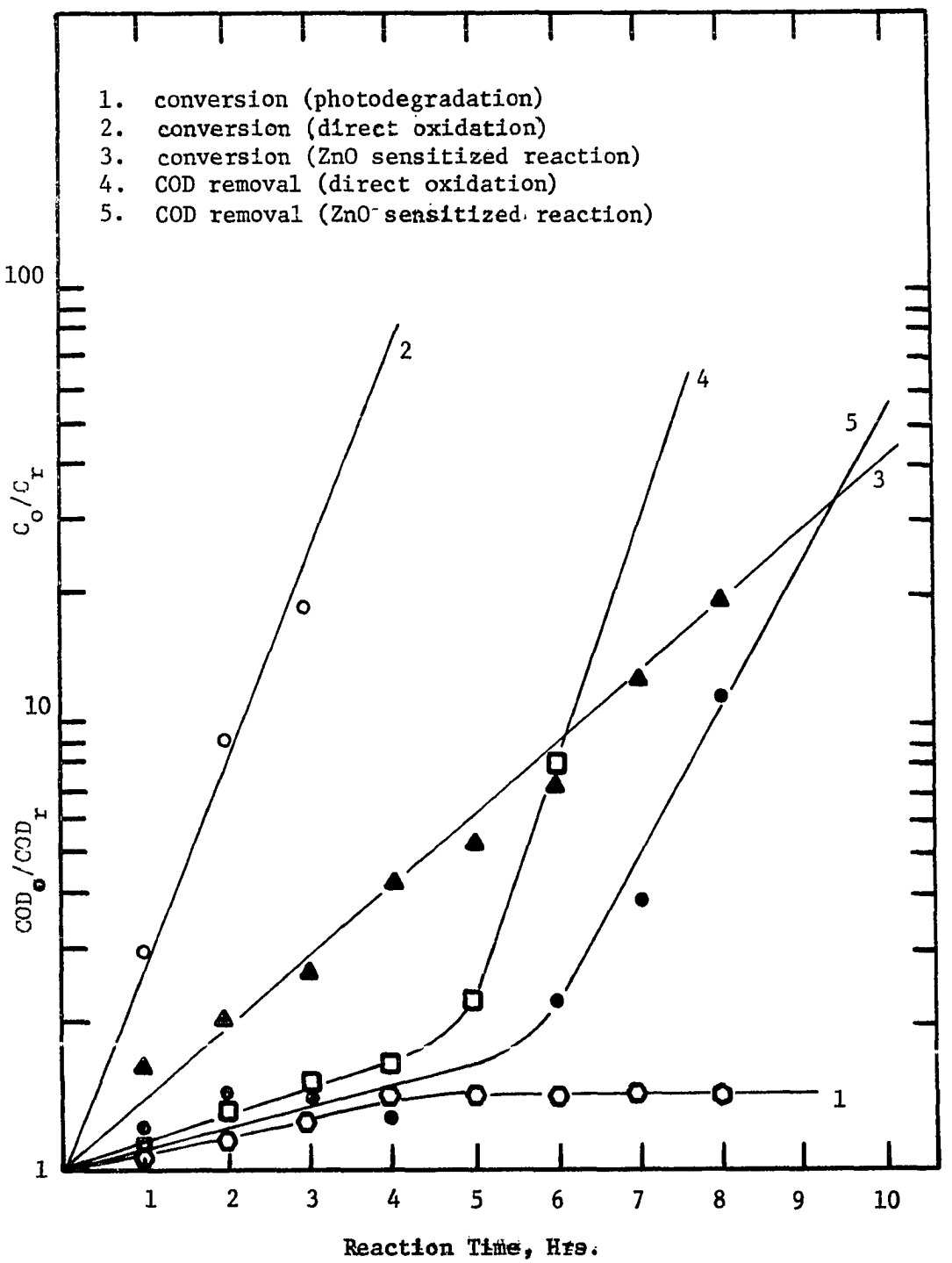


Figure 8. The Extent of Photodegradation, ZnO Sensitized and Direct Photooxidation of Aqueous Solution of Phenol, 500 mg/1.

phenol is degraded, the deactivation of the activated species or radicals is as fast as the rate of degradation. Hence, the net result of the reaction is negligible, or cannot be detected analytically.

Assuming that the theoretical minimum energy to break all the bonds in one mole of phenol equals the total bond energies as given in the literature. The energy then required will be:

$$\begin{aligned} 5 \ \text{C-H} &= 5 \times 99 \\ 3 \ \text{C-C} &= 3 \times 83 \\ 3 \ \text{C=C} &= 3 \times 147 \\ 1 \ \text{C-O} &= \underline{3 \times 84} \\ &\quad 1269 \ \text{Kcal/mole} \end{aligned}$$

Considering that phenol has a maximum absorption peak at 2780 Å and below 2380, and the UV lamp used emits a total of approximately 3.4 watts or 3.4 Joule, it is then possible to calculate theoretically the time needed to break all the bonds of 500 mg/l phenol in the aqueous solution.

$$500 \ \text{mg/l} = 5.35 \times 10^{-3} \ \text{mole/l}$$

This corresponds to the required theoretical fission energy of 6.75 Kcal. The energy available is;

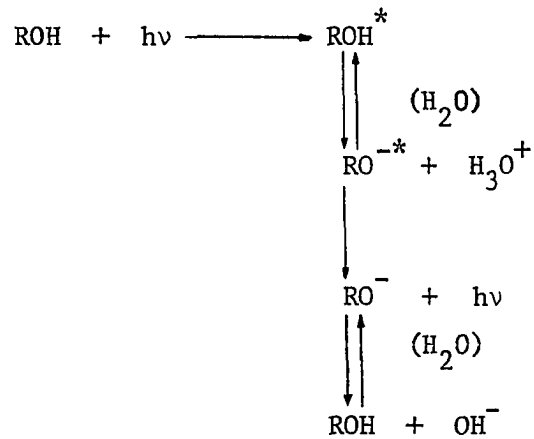
$$3.4 \ \text{Joule/sec} = 8.126 \times 10^{-4} \ \text{Kcal/sec.}$$

hence, the theoretical time required, assuming 100% efficiency, for total breakdown is:

$$6.75 \div 8.126 \times 10^{-4} = 8306 \ \text{seconds or } 138 \ \text{minutes}$$

Suppose that 75% of the radiated energy is absorbed by the immersion well, cooling water, etc. Then, 552 minutes or 9.2 hours will be sufficient to destruct all the bonds in 500 mg/l phenol. Comparing this theoretical value to the result obtained, it is very obvious how ineffective the photodegradation process is.

The ineffectiveness of this process is believed to be incorporated in the deactivation of the activated species or radicals. The mechanism of the deactivation reaction is given by:



where: R = phenyl.

The low conversion of phenol by photodegradation does not result in a measurable change in the total oxidizable organic, COD. This indicates that the disappearance of the substrate, as measured by the remaining phenol concentration, was primarily due to the change in the chemical structure as a result of the cleavage of one or two bonds without forming any gaseous products, i.e. CO, CO_2, CH_4, etc.

The rate of conversion of phenol by ZnO sensitized oxidation is much faster than by the previous mentioned process. The reaction follows a first order kinetics with respect to the substrate. According to Markham and Laidler [31], the ZnO sensitized oxidation of phenol results in the destruction of the aromatic ring. The yellowing of the solution is assumed to be due to the formation of humic acid compounds.

The removal rate of the oxidizable organic by ZnO sensitized oxidation is represented by line 5 of Figure 8.

In the interpretation of the rate data in terms of COD removal an

assumption has to be made, i.e. the reaction products are CO, CO_2 or other compounds that will not remain in solution. This assumption is justifiable on the grounds that the final products of any oxidation process are generally CO_2, CO or other stable low molecular weight oxy-compounds. In the event the above assumption is true, then the change in COD will be directly related to the change in the corresponding substrate that exerts COD.

There is another possibility to be considered. The decrease in COD is not caused by the reduction of the oxidizable matter in the system, but by the low COD exertion rate of the reaction product. In the case of phenol oxidation that possibility can be excluded on the basis of the knowledge that the photooxidation process of this organic involves breaking of the aromatic ring and consequently, the products are amenable to chromate oxidation.

The reaction mechanism of ZnO sensitized oxidation of phenol is well established by Markham and Laidler [31].

The plotting of the data (Figure 8) shows that at the beginning, the reaction proceeded at a slow rate and may be correlated to the destruction of the aromatic ring. The reaction would then proceed at a faster rate and would usually be accompanied by the disappearance or reduction of the color. It is reasonable to consider that the reactions involved in this process consist of a series of first order reactions as indicated in Figure 8 by the straight line portion having different slopes, reaction rate constant.

The rate of conversion of phenol by direct photooxidation is much faster than that of ZnO sensitized oxidation. The reaction is apparently first order with respect to the substrate. Visually, the reaction was

similar to sensitized oxidation in regard to the yellowing of the solution and disappearance of the color under prolonged exposure.

For a direct photooxidation reaction involving irradiation with UV light, the rate of COD removal is relatively faster than that achieved by a ZnO sensitized reaction. Referring to the reaction scheme outlined by Young, et. al. [17], the disappearance of substrate, A, is represented by:

$$-\frac{dA}{dt} = I_o \varepsilon [A] \ (1-\phi_F) \ \frac{k_{rx(1)}}{kd}$$

Under one reaction condition, the term:

$$I_o \varepsilon (1-\phi_F) \ \frac{k_{rx(1)}}{kd}$$

can be considered constant, hence:

$$-\frac{dA}{dt} = k'[A]$$

represents a rate equation of first order reaction.

However, as the reaction proceeds, the intermediate product AO_2 will be further photolyzed and the reaction scheme may or may not go via the same route. Although the reaction might follow first order kinetics, one cannot expect that the reaction rate constant, k', will remain unchanged because of possible successive or parallel reactions occurring in the system. The increase or decrease of k' will depend on the nature of the oxygenated product, AO_2. If the intermediate product, which can be a peroxide or hydroperoxide, is very susceptible to physical or chemical fragmentation or decomposition, then in prolonged irradiation one can expect that k' increases.

In Figure 8, line 4, it can be observed that the reaction involving COD removal is slow at the early stages of the process. This can be interpreted that the controlling reaction at that period of time is the

formation of the oxygenated product, AO_2. Subsequently, the intermediate is photolyzed and the change in the slope indicates that the product is more amenable to photooxidation or photodegradation, which brings about a fast reduction of the oxidizable compounds. For phenol, the abrupt change of the reaction rate is accompanied by the disappearance of color. This can support the hypothesis that the oxygenated products are more amenable to photooxidation than the substrate itself. It is also possible that reduction of color, as a result of destruction of the chemical(s) involved, makes the blocking of light penetration insignificant and hence, sufficient energy is available for further destruction of the intermediates.

The effect of pH on the extent of direct photooxidation can be seen in Figure 9. It is obvious that a low pH has a substantial effect on the course of the reaction as indicated by the sudden change in rate constant, slope of the line. Applying the simplified approach as mentioned earlier, there is a tendency for the reaction to proceed at a faster rate at low pH than at high pH. There are two possibilities that this can be attributed to:

1. The system itself --particularly the light source. If the lamp needs a considerably long time, 4-5 hours, to reach its maximum intensity, and the rate of disappearance of the substrate is dependent on the intensity, then naturally that condition will effect the reaction. To check this, the experiments were repeated under the same conditions, except in one trial when the lamp was on for about 5 hours before the substrate was introduced into the reactor. Plotting of the obtained data is given in Figure 10.

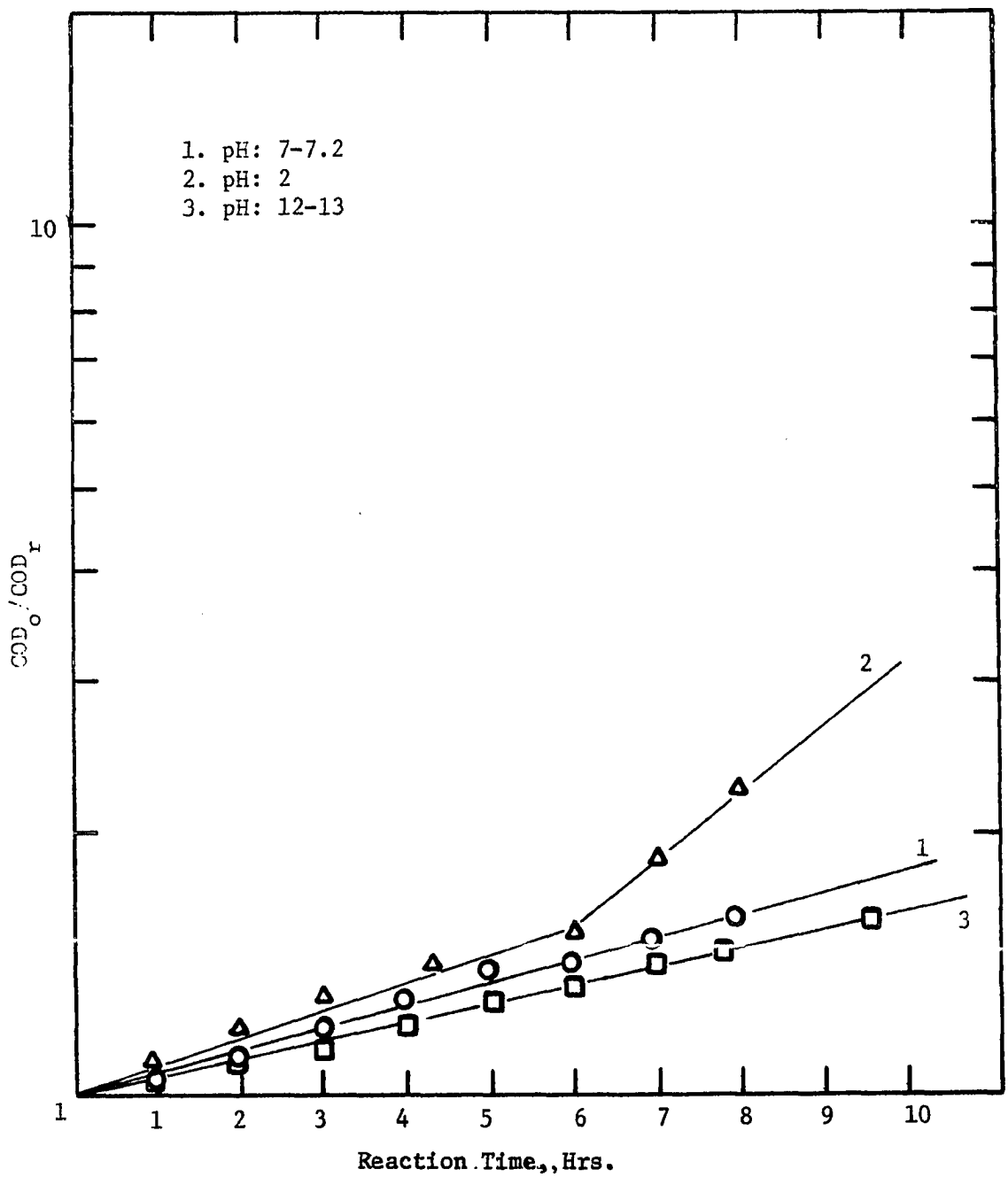


Figure 9. The Effect of pH on the Extent of Direct Photooxidation of Aqueous Solution of Phenol, 1000 mg/l.

2. If the reaction products are CO_2 and other acid soluble compounds, then according to the Le Chatelier principle, at low pH the reaction as written will go to the right in favor of the decomposition of the products at a faster rate than under neutral or alkaline conditions.

$$P + O_2 \xrightleftharpoons{h\nu} PO_2 \xrightleftharpoons{h\nu} \text{Products} + CO_2$$

$$\text{Products} + O_2 \xrightleftharpoons{h\nu} CO_2 + \text{another product, etc.}$$

Unfortunately, this hypothesis cannot be confirmed due to the difficulty in trapping and anlyzing the gaseous product(s).

The effect of initial concentrations to reaction rates in terms of COD removal is presented in Figure 11.

Referring to the discussion by Young, et. al. [17], and considering the reaction kinetics of singlet oxygen formation given by the expression [15]:

$$\phi_{AO_2} = {}^{\phi}3_{Sens} \frac{k_2[A]}{k_1 + k_2[A]}$$

at high concentrations of A, the equation reduces to:

$$\phi_{AO_2} = {}^{\phi}3_{A_1}$$

where:

A = substrate

AO_2 = oxygenated product

${}^3A_1$ = substrate at triplet state

This relationship implies that the rate of formation of AO_2, or disappearance of substrate A, is determined by the rate of formation of ${}^3A_1$.

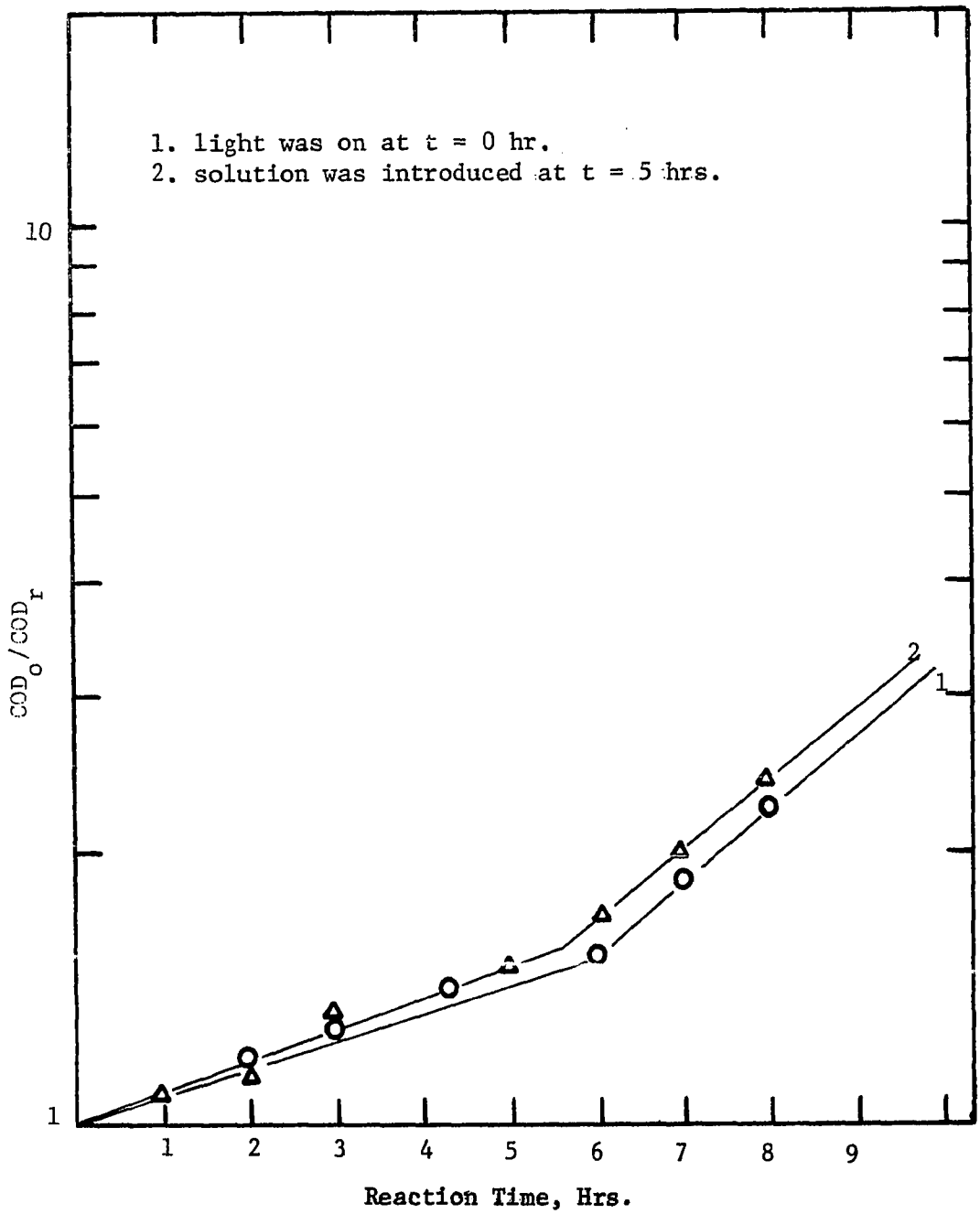


Figure 10. The Effect of Light Source on the Extent of Direct Photooxidation of Aqueous Solution of Phenol, 1000 mg/l, at pH 2.

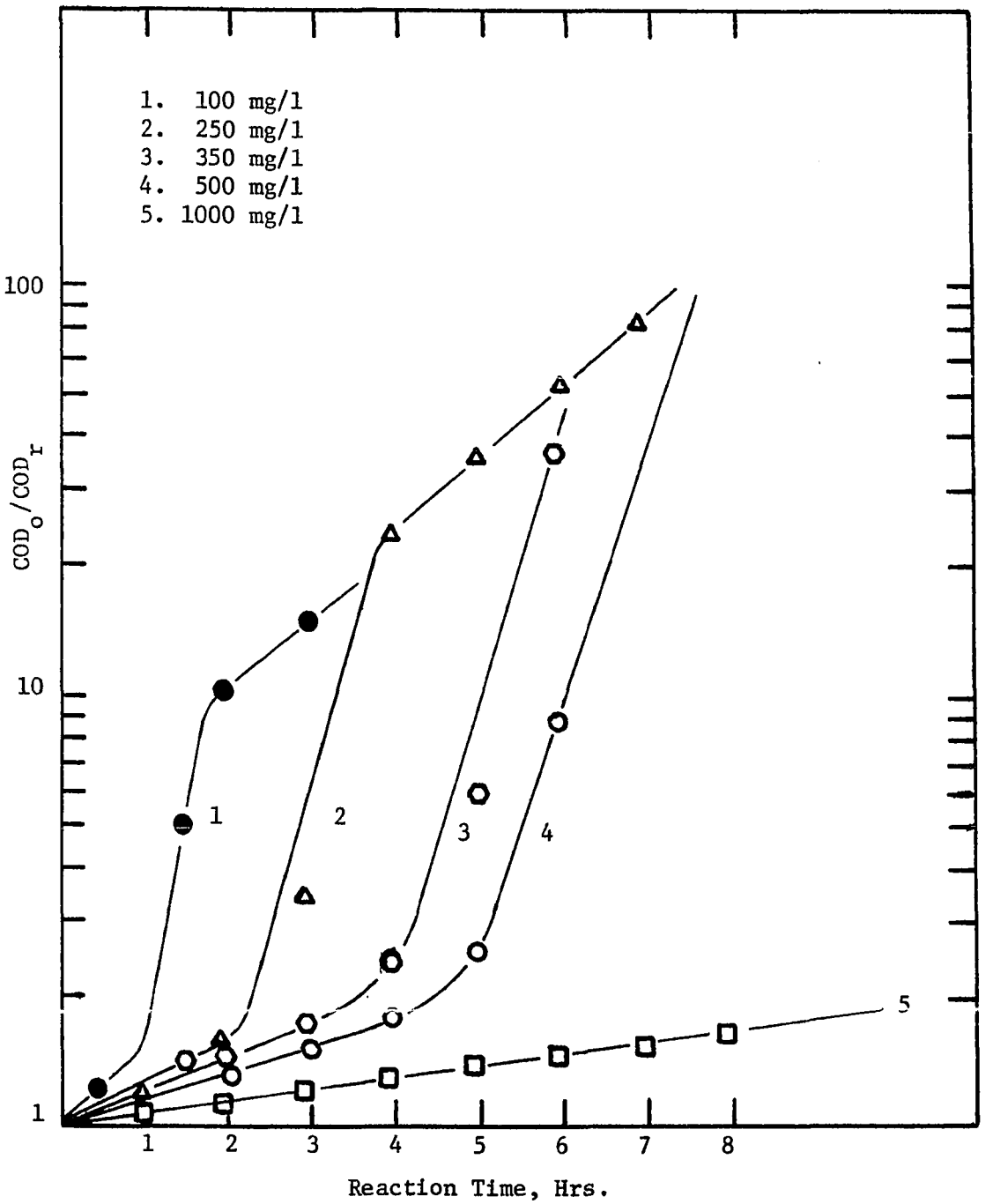


Figure 11. Extent of Initial Concentrations on the Extent of Photo-oxidation of Aqueous Solution of Phenol, 100 mg/l-1000 mg/l.

Kaske and Lindqvist [20] have studied the reaction of the sensitizer triplet state. Based on the mechanisms as discussed in Chapter II, it is reasonable to assume that at high concentrations of substrate A, the sensitizer, and under constant light intensity, the concentration quenching reaction will become important. Consequently, the overall rate constant of direct photooxidation will not be independent on initial concentrations.

The plotting in Figure 11 indicates that at a high concentration, 1000 mg/1, the reaction follows first order, or more precisely pseudo-first order kinetics, based on the data obtained within the experimental reaction time. At a lower concentration, 100-500 mg/1, the photooxidation of aqueous phenol is neither simple first order nor simple second order, as conclusively indicated in Figures 11 and 12.

Due to present knowledge and experimental data, it is difficult to give a satisfactory interpretation for the S-type curve as shown in Figure 11. However, a partial and qualitative explanation for this phenomenon could be found by relating the process to the nature of the intermediate or reaction product.

Photooxidation of low molecular weight alcohols and acids, as will be discussed later, may throw some light on the nature of the oxidation of phenol. It is assumed that the photooxidation of phenol is coupled by fragmentation, followed by subsequent oxidation of the fragments, intermediates. As the reaction proceeds to the final stage, the oxidizable organics are mostly low molecular weight fragments. The slowness of the reaction is measured by the low reaction rate constant which reflects the susceptibility of the compound(s) to photooxidation. This explanation is based upon the similarities of photolysis of aqueous methanol.

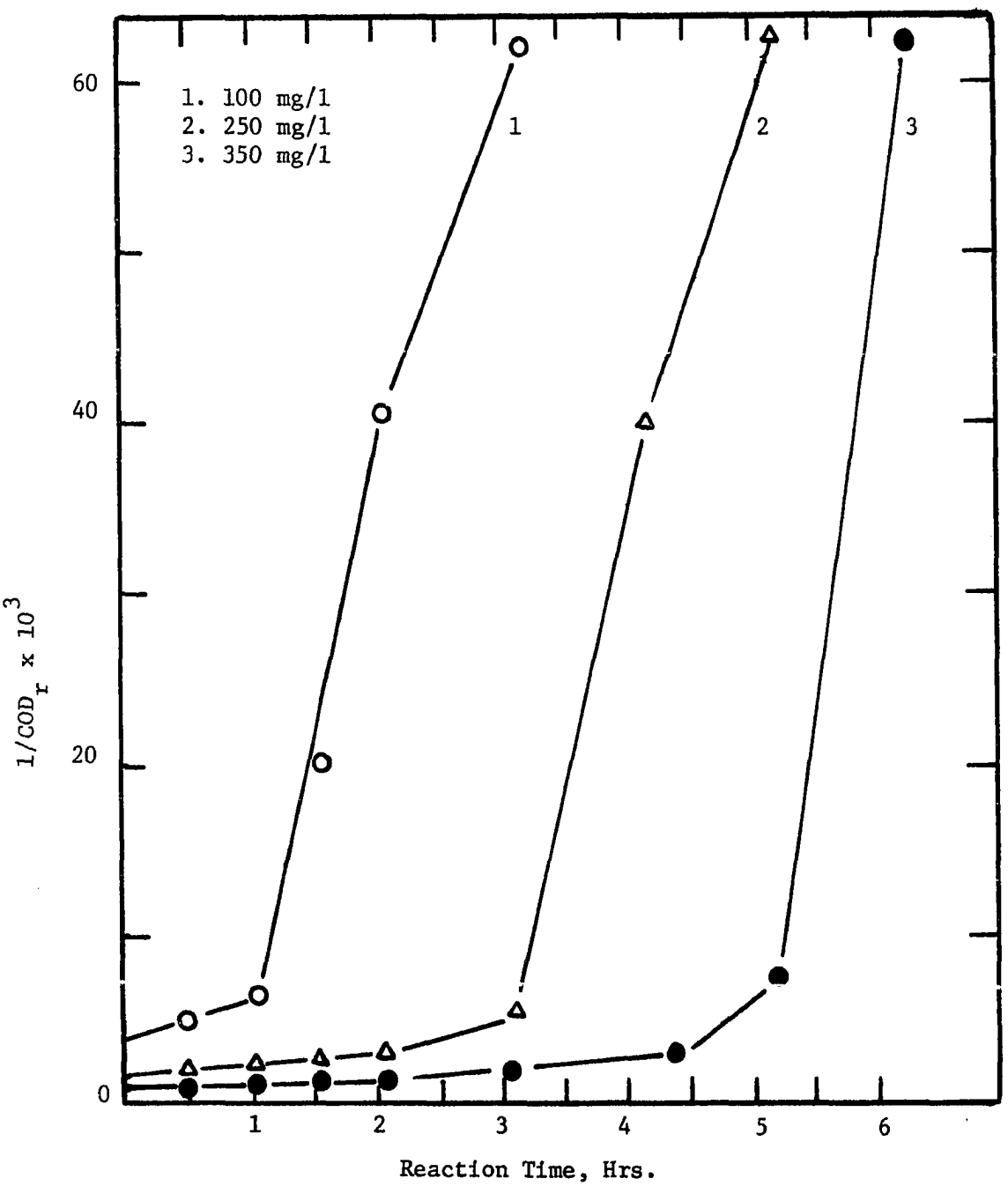


Figure 12. The Effect of Initial Concentration on the Extent of Photooxidation of Aqueous Solution of Phenol.

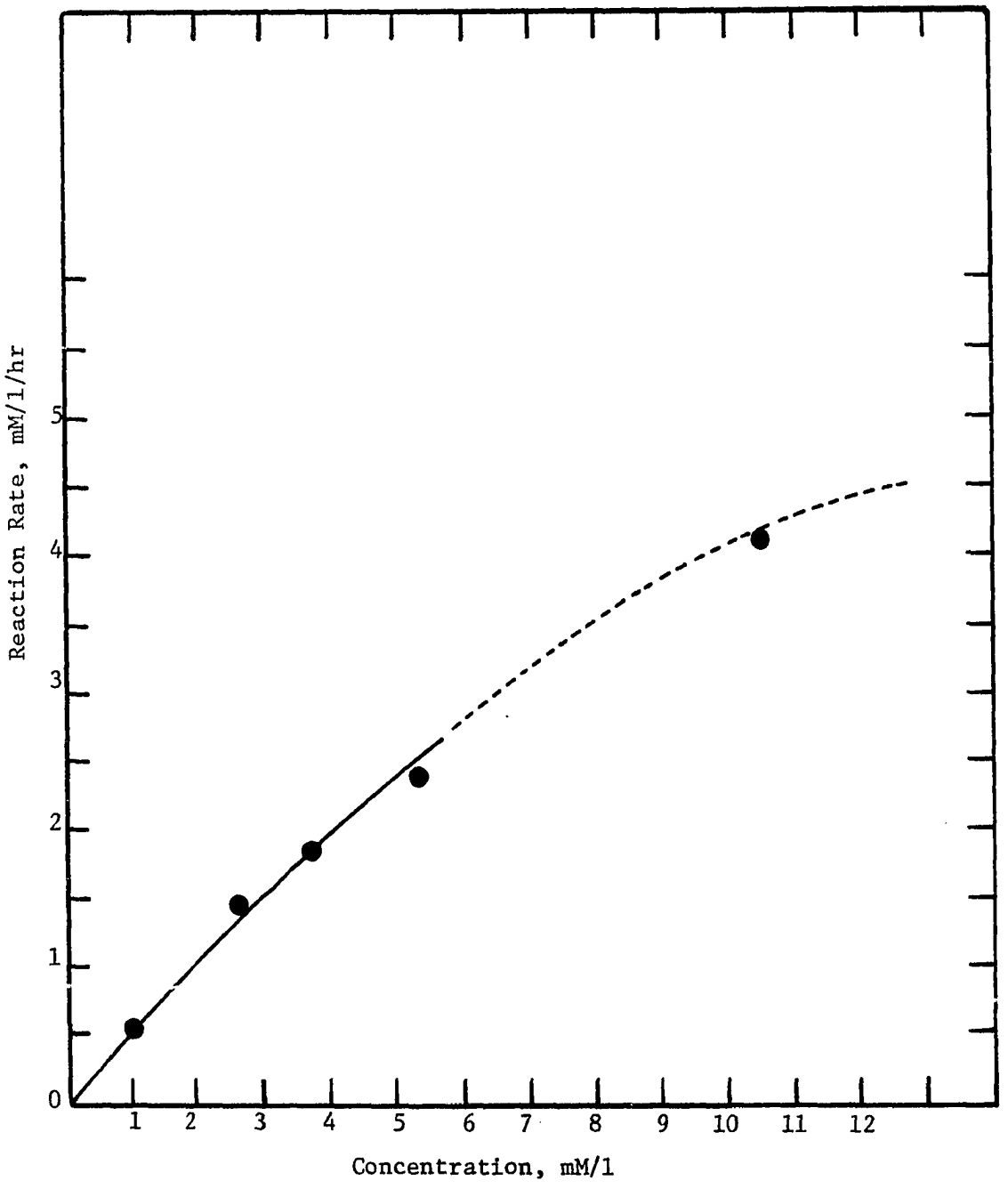


Figure 13. The Effect of Initial Concentration on the Reaction Rates of Photooxidation of Phenol in Aqueous Solution.

If the process does consist of successive first order reactions, and if the overall reaction rate constant is estimated by taking the average value calculated from:

$$k_{avg.} = k_i \times t_i : t_{Total}$$

where:

t_i = the reaction time corresponding to the straight line portion with slope;

k_i = the first order reaction rate constant,

t_{Total} = the time required for complete oxidation.

Then, by plotting the reaction rate as explained by:

$$-dC/dt = k_{avg.} C$$

vs. initial concentration, C, gives the curve as shown in Figure 13. The last point of this curve was estimated by extrapolation and is understood to be slightly over-estimated. In spite of this, the line shows a decline trend at high concentrations, indicating that there must be a maximum concentration beyond which the reaction rate will drop substantially. It is also reasonable to assume that the maximum concentration will strongly depend on the process conditions and on the compound itself.

To support the above proposition, the experimental data were plotted in different ways. Figure 14 represents the plotting of the rates of COD removal during the first hour of the process vs. initial concentrations. Figure 15 plots the change of COD per unit time vs. reaction time for different initial concentration. This qualitative evaluation strongly suggests that the reaction rate in direct photooxidation will not increase unlimitedly as the concentration increases as has been predicted by other investigators [23].

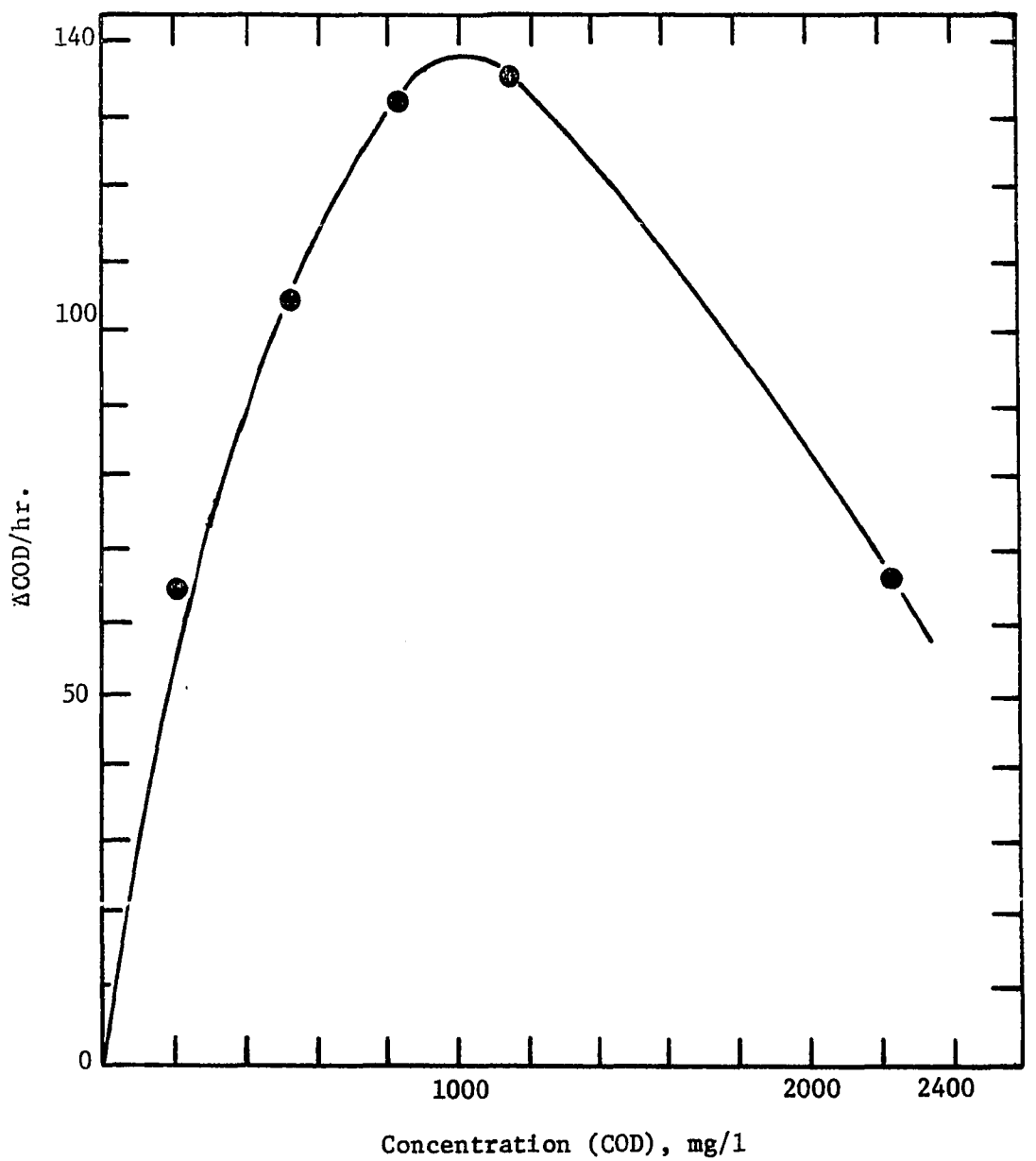


Figure 14. The Effect of Initial Concentration on the Removal Rate During the First Hour of Reaction.

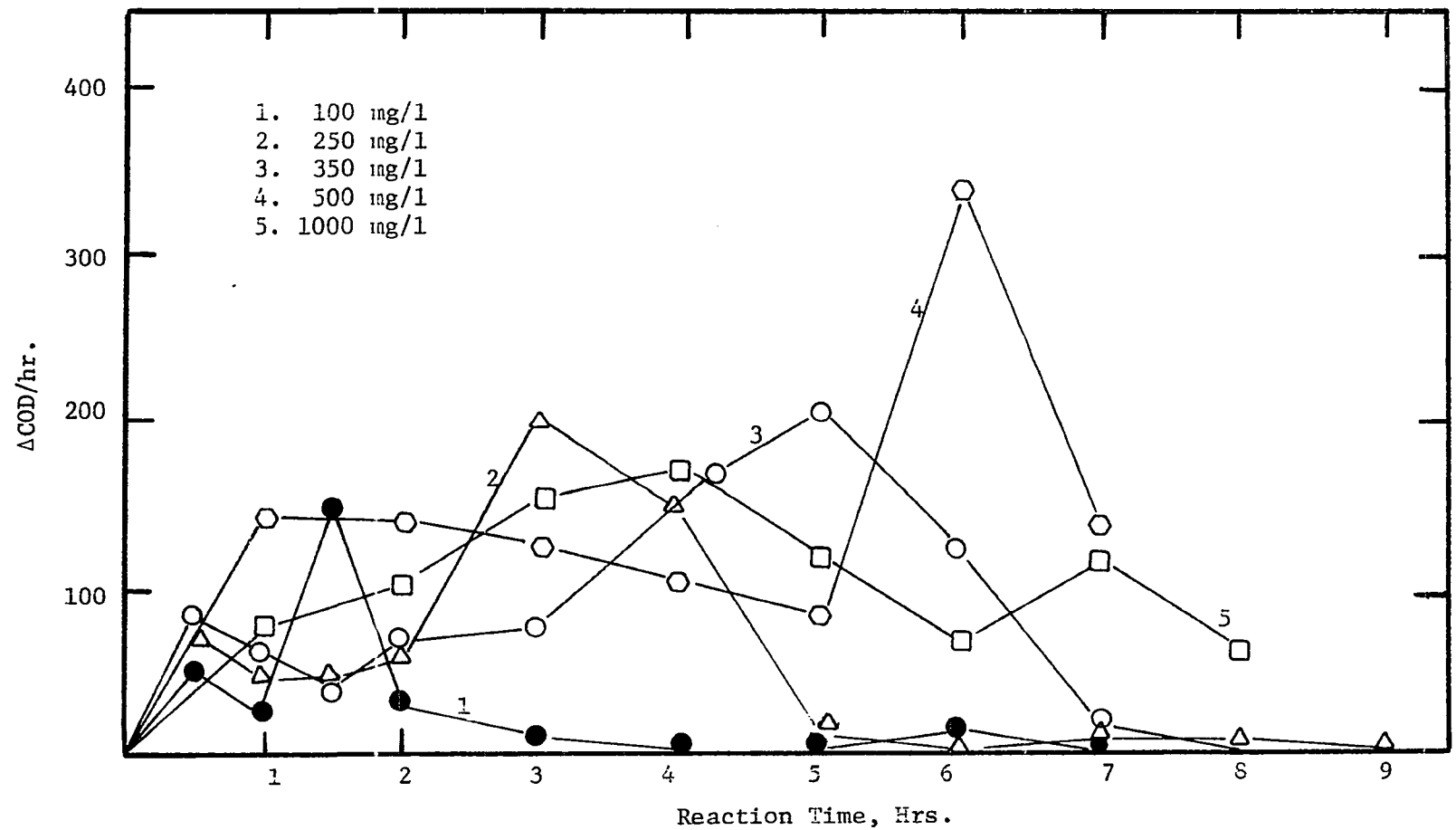


Figure 15. The Rate of COD Removal for Different Initial Concentrations of Aqueous Phenol Solutions.

Recalling Equation 9, page 62, the relationship implicitly shows an increase in A concentration will result in the increase in the corresponding reaction, k_I. Substituting k_{avg} for k_I and plotting the average values of the reaction constant vs. initial concentration, produces a line with a negative slope. This indirectly implies that the photooxidation of phenol in aqueous solution cannot be assumed as a first order reaction with respect to the reactant.

The BOD reduction of the irradiated phenol solution is not consistent. Without knowing the constituent(s) present in the solution, it is impossible to explain the inconsistency of the BOD reduction as a function of time. The fluctuation of BOD values might be due to some toxic materials formed in the reaction step. Photooxidation of the toxic compound(s) could change the toxicity and hence, the BOD measured would be higher than the previous one. One obvious point is that BOD is generally less than COD, or the BOD/COD ratio is less than unity. This data is shown in Figure 16.

Cyclohexanone.

The result of the photodegradation and direct photooxidation of cyclohexanone in aqueous solution indicates that this compound undergoes photochemical reaction quite readily. The chromatogram did not show the presence of a ketone after an irradiation of 60 minutes. The modes of photodecomposition of cyclic ketones have been interpreted by various workers [8,19], and generally the reaction is very dependent on the condensed or gaseous phase of the system and the nature of the solvent. In aqueous solution the possible reation [19] is:

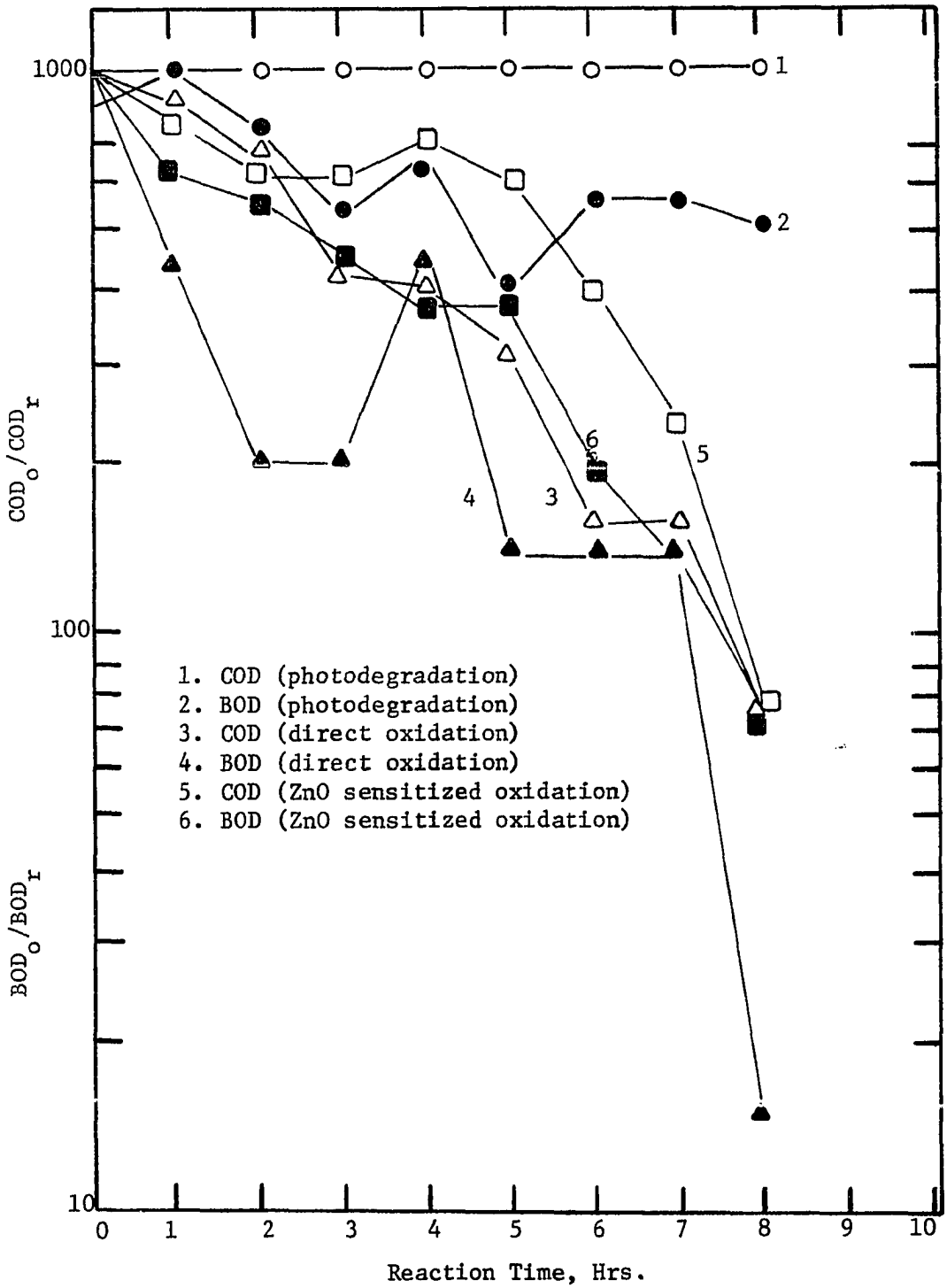
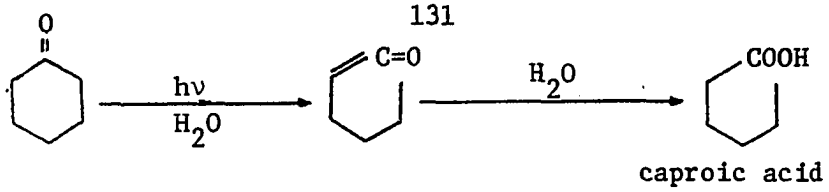


Figure 16. The Extent of Photodegradation, Direct Photooxidation and ZnO Sensitized Oxidation of Phenol in Terms of COD and BOD Reductions.



caproic acid

with caproic acid as the major product.

The disappearance of cyclohexanone in the irradiated solution did not result in the reduction of COD, indicating that the reaction did not involve the formation of CO as given elsewhere [8,19]. The failure of this process to reduce the COD is not surprising if the reaction is limited to transformation of the ketone to caproic acid. Caproic acid is fairly soluble in water and has six carbon atoms as does the ketone. Therefore, the theoretical COD values of both compounds are approximately the same. Consider the reaction:

$$(CH_2)_5\text{-}CO + h\nu \xrightarrow{+H_2O} CH_3(CH_2)_4COOH$$

ketone acid

Assuming that x mg/l cyclohexanone is converted to caproic acid, then, x/M milli-mole of caproic acid will be formed. The theoretical COD values for both compounds can be calculated from the following stoichiometric equations:

$$\text{ketone: } (CH_2)_5\text{-}CO + 8O_2 \longrightarrow 6CO_2 + 5H_2O$$

$$\text{acid: } CH_3(CH_2)_4COOH + 8O_2 \longrightarrow 6CO_2 + 6H_2O$$

The above equations suggest that both compounds use the same amount of oxygen. Any difference that may appear in the COD tests can be related to the susceptibility of the corresponding compound.

After prolonged irradiation, a photodegradation process could bring about a slight reduction in COD from the solution. It is believed that

the caproic acid which was formed as an intermediate is photolyzed, coupled by fragmentation and formation of CO_2 or CO. The extent of these photochemical reactions of aqueous cyclohexanone is shown in Figure 17.

The deactivation reactions cannot be responsible for the slowness in the reduction of the oxidizable organic. If this were true, the conversion rate or disappearance of the ketone would also be slow.

The conversion of cyclohexanone by ZnO photosensitized oxidation is much slower than that of direct photooxidation or photodegradation. In retrospect, this is not surprising as the first absorption region of the ketone is 2400-3200 Å, with λ_{max} = 2900 Å. The borosilicate immersion well which was used for this experiment absorbed a substantial portion of the short wavelengths. Consequently, the available energy necessary for the process to occur is much less than in the other two systems, where a quartz immersion well was used. Hence, the rate of conversion is retarded significantly.

No information could be found to describe the reaction steps involved in the reduction of the oxidizable organic(s) in this ZnO sensitization process. Based on the nature of the ketones and the generalized photosensitized oxidation mechanism, it is reasonable to assume that the oxidation produced a fission at the C-CO bond, followed by the formation of organic acids, peroxides or hydroperoxides.

The rate of removal of the oxidizable organic compound(s) by ZnO photosensitized oxidation is apparently very slow. Except for shorter lag, the rate is of the same magnitude as that of photodegradation. Assuming hydrogen peroxide to be the only oxidizing species in this system, the relative low reaction rate is actually inherent to the oxidation

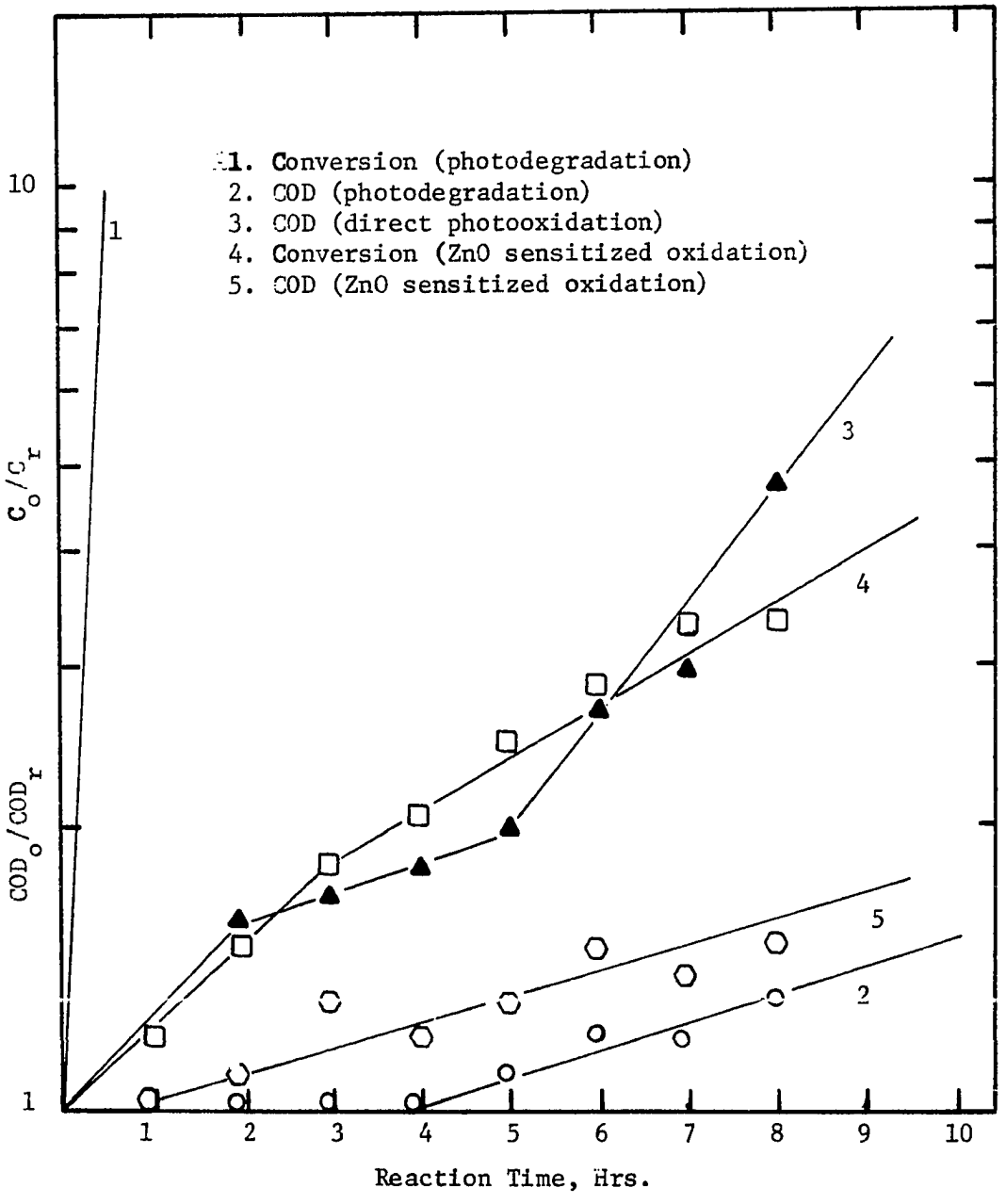


Figure 17. The Extent of Photodegradation, Direct Photooxidation and ZnO Sensitized Oxidation of Cyclohexanone in Aqueous Solution Measured in Terms of COD and Rate of Conversion.

characteristic of the peroxide. As disclosed by Bishop [4], hydrogen peroxide oxidized an appreciable portion of refractory material in the presence of ferrous-ferric catalyst and at an optimum pH of 3-5. In the ZnO sensitization process the pH was 7, slightly higher, and the appropriate catalyst was not present. Therefore, it is conceivable that the reaction proceeds more slowly. This is of course, a partial explanation, but considering the other experimental results it can be concluded that ZnO photosensitized oxidation is not an effective process in reducing the oxidizable organics measured by COD.

The rate of disappearance of cyclohexanone by direct photooxidation is in the same order of magnitude as that of the photodegradation process. Considering that the physical conditions of both processes are the same, it is justifiable to assume that the primary process involved is responsible for the destruction of the cyclohexanone. Hence, the rates of conversion for the two photo-processes are approximately equal.

Comparing the other two previously mentioned processes, photodegradation and ZnO sensitized oxidation, direct photooxidation of cyclohexanone in aqueous solution substantially reduces the COD. The data plotted, i.e. COD_o/COD_r vs. time or $1/COD_r$ vs. time, reveals that the reactions are not simple first or second order (Figures 18 and 19). In interpreting the data, it is reasonable to speculate that the reactions consist of a sequence of pseudo first order reactions.

The mechanisms of this process is not known. But one can theorize the probable reaction paths, but assuming:

1. The absorption of photons results in the formation of caproic acid, $CH_3(CH_2)_4COOH$;

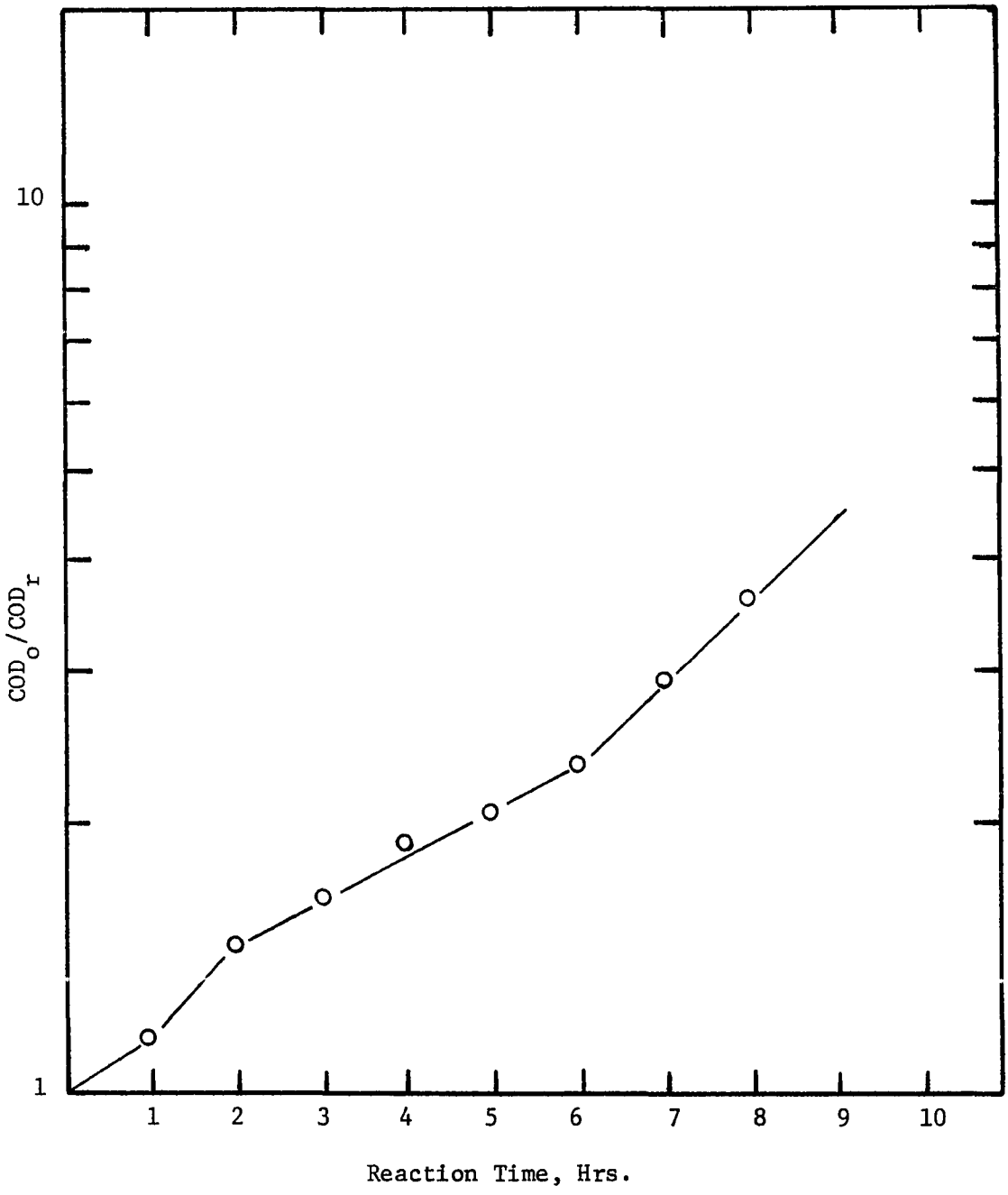


Figure 18. The Extent of Direct Photooxidation of Aqueous Solution of Cyclohexanone, 1000 mg/l, in Terms of COD Reduction.

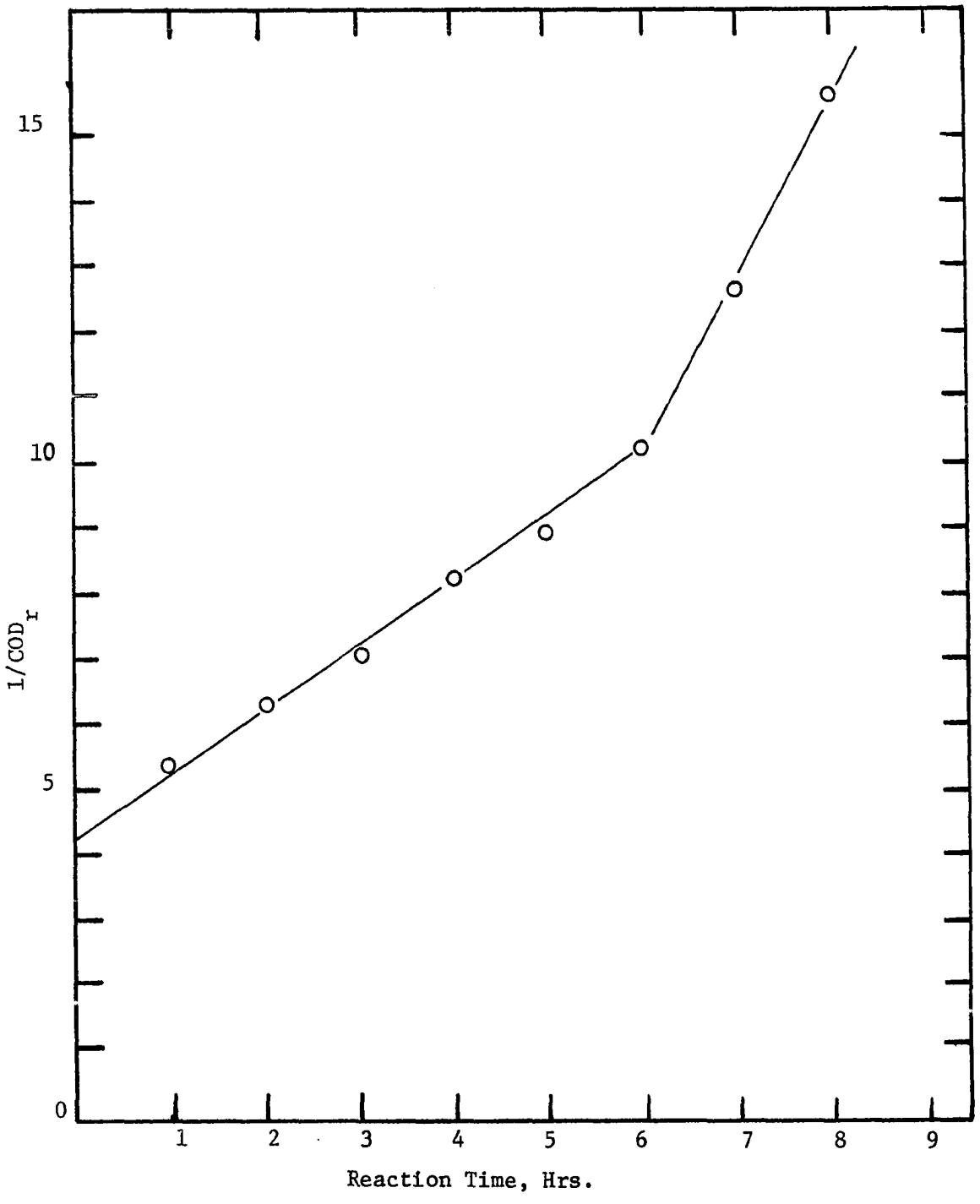


Figure 19. The Extent of Direct Photooxidation of Aqueous Solution of Cyclohexanone, 1000 mg/1, in Terms of Cod Reduction.

2. The subsequent reaction involves the oxidation of the acid to peracid which in turn undergoes decomposition.

Then:

$$R\text{-}COOH \xrightarrow{h\nu, O_2} R\text{-}COOOH \longrightarrow ROH + CO_2$$

$$R\text{-}COOOH \longrightarrow R\cdot CO\cdot OH + \tfrac{1}{2}O_2$$

$$ROH \xrightarrow{h\nu, O_2} R'COOH \xrightarrow{h\nu, O_2} R'COOOH \longrightarrow R'OH + CO_2$$

$$R\cdot CO\cdot OH \xrightarrow{h\nu} RCO^{*} + OH$$

The effect of pH on the direct photooxidation of cyclohexanone is given in Figure 20 and similar phenomenon of phenol has been observed. The high OH^- concentration may account for the retardation of the formation of caproic acid, or the enhancement of other reaction(s) which affect the overall reaction sequence.

The reduction of COD as the result of the carboxylation of caproic acid is very improbable under oxidation condition.

$$2CH_3(CH_2)_4COONa + OH^- \longrightarrow 2CH_3(CH_2)_3CH_3 + Na_2CO_3$$

If possible OH^- could be expected to enhance the COD reduction process.

At neutral and acid conditions the reaction follows the same trend, but in the latter condition the reaction seemed to be significantly enhanced by the presence of hydrogen ions. Whether this is related to the occurrence of a reaction involving the formation of CO_2 --which according to Le Chatelier will be affected by H^+-- was not not confirmed experimentally.

The effects of initial cyclohexanone concentration on the extent of the reaction was not studied because the results were expected to be analogous to phenol or hexylalcohol. The magnitude of the effect may be

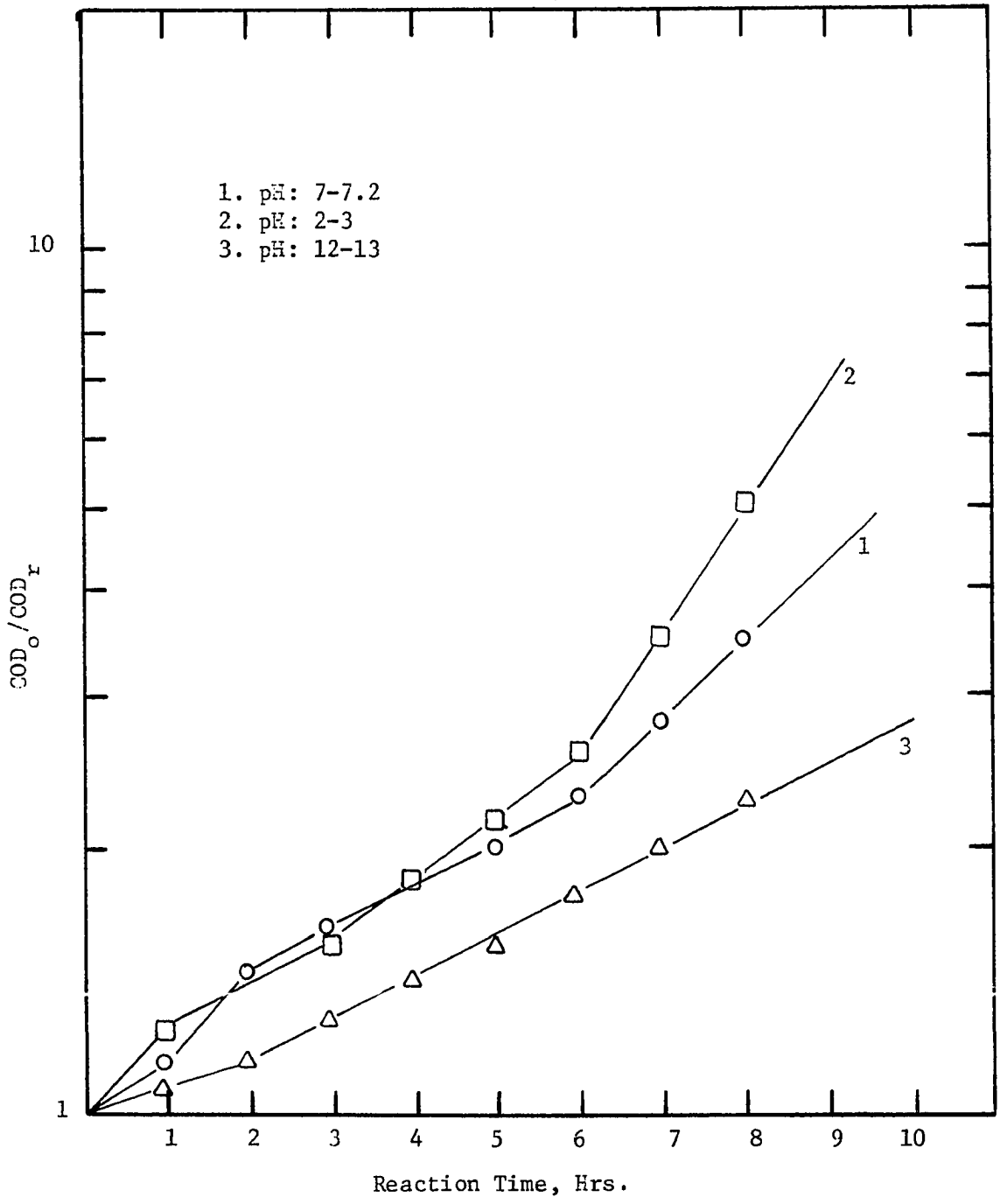


Figure 20. The Effect of pH on the Extent of Direct Photooxidation of Aqueous Solution of Cyclohexanone, 1000 mg/l.

different but the concentration quenching reaction, which is assumed to be the controlling factor, will undoubtedly change the course of the overall reaction.

Hexyl-Alcohol

As disclosed by the preliminary experiments (Appendix D, Table D-3), hexanol was not susceptible to photodegradation under the reaction conditions applied to the system, 550 watt high-pressure lamp. The conversion by irradiation was not significant and so no further attempt was made to study the extent of this process.

The ineffectiveness of photodegradation using a 550 watt high-pressure lamp is primarily due to the lack of sufficient energy for the molecule to undergo a photo-reaction. In general, alcohols have an absorption band below 2000 Å. Since the lamp radiates 2200 Å and above wavelengths, it fails to induce the reaction.

The mode of photodecomposition of a normal alcohol is well known and has been studied by many workers. The absorption of photons will lead to the formation of radicals and the cleavage of the molecule. The reaction route or products will be strongly dependent on the alcohol, conditions of the system, gaseous or condensed, and the available energy.

Due to the lack of sufficient energy for the formation of the excited state hexanol, the reaction mechanism of photooxidation as proposed by Young [17] or Gollnick [14] cannot be applied directly to the photooxidation of hexanol. The reaction can be assumed to be initiated by autoxidation, i.e. oxidation by oxygen at its ground state, which results in the formation of an acid or an oxy-compound that has an absorption band above 2200 Å. This acid can then be photooxidized and the reaction may follow

the generalized route as suggested by several investigators [8,19]. If this reaction takes place as postulated, then one would expect that a lag must exist because autoxidation is usually a slow process. However, the plotting of the conversion data (Figure 21) shows that the reaction follows a first order, or more like a pseudo first order kinetics without any observable "induction time". The absence of the lag suggests that the photooxidation of hexanol by direct irradiation is not initiated simply by autoxidation, but other reactions, such as chain or autocatalytic reactions, may contribute to the overall process.

Referring to Figure 21, it is very obvious that the rate of conversion of hexanol by ZnO sensitization reaction is substantially lower than that by direct photooxidation. Again, the explanation lies in the oxidizing nature of hydrogen peroxide as previously discussed.

The removal of the oxidizable organics (COD) by the ZnO sensitized oxidation is apparently less effective in comparison to that achieved by direct photooxidation. In an eight hour reaction, only 44% COD was removed as compared to 80% by direct photooxidation.

The reaction scheme of this particular process, i.e. ZnO sensitized reaction or direct photooxidation of hexanol, is not known. The decomposition of the formed hydroperoxide at its O-O bond has to be excluded, as this will not result in a measurable change in COD of the solution irradiated.

Suppose that the residual organics are quantitatively measured by a COD test. Then the reduction in COD must be related to the fragmentation of the compound into CO, CO_2 and other gaseous products. The formation of CH_4, C_2H_6 or other saturated/unsaturated low molecular weight hydrocarbons

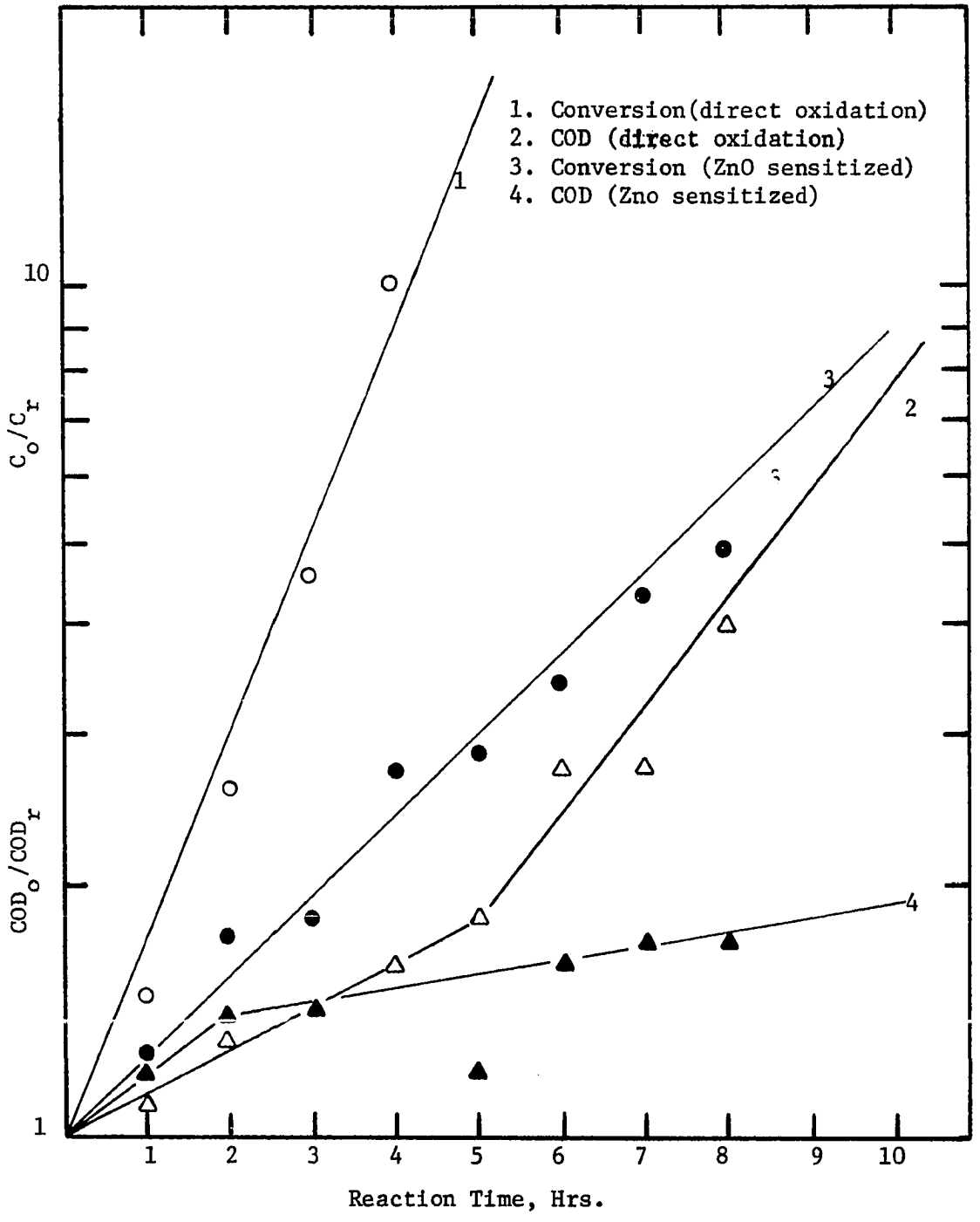


Figure 21. The Extent of Photooxidation and ZnO Sensitized Oxidation of Aqueous Solution of Hexanol, 820 mg/l, Measured in Terms of COD and Rate of Conversion.

is theoretically not possible under oxidation conditions as these compounds have lower oxidation states than alcohols. If CO or CO_2, or both, are the major products, then the first oxidation product has to be the corresponding acid which can undergo photodegradation, or direct photooxidation, according to the reactions described earlier in this chapter. The product of this subsequent reaction can be peracid which decomposes into CO_2 and alcohol, with one carbon atom less than the original compound. The alcohol will then be further oxidized following a similar or different route. Regardless of the reaction scheme it follows, the process must involve fragmentation that can bring about reduction in COD.

The effect of initial concentration on direct photooxidation of an aqueous solution of hexanol is illustrated in Figure 22. The plotting of the experimental data depicts striking similarity that obtained from the irradiation of phenol. There is one exception that is not well understood. The complete oxidation of 205 mg/l hexanol could be achieved in 4 1/2 hours as compared to 5 1/2 hours for a concentration of 82 mg/l. Satisfactory explanation could not be found and experimental error has to be excluded since repeating the experiment provided the same results.

In spite of the deviation from the general trend there is a consistency --the presence of a lag at the beginning of the reaction. The explanation of this lag can be approached from the nature of autoxidation, which is characterized by its slowness, as a result of its low reactivity of triplet ground state molecular oxygen to a singlet state substrate.

Figure 23 shows the effect of pH on the photooxidation of hexanol. The rate of reaction in acid and neutral conditions can be considered to be the same order of magnitude. The high hydrogen ion concentration did

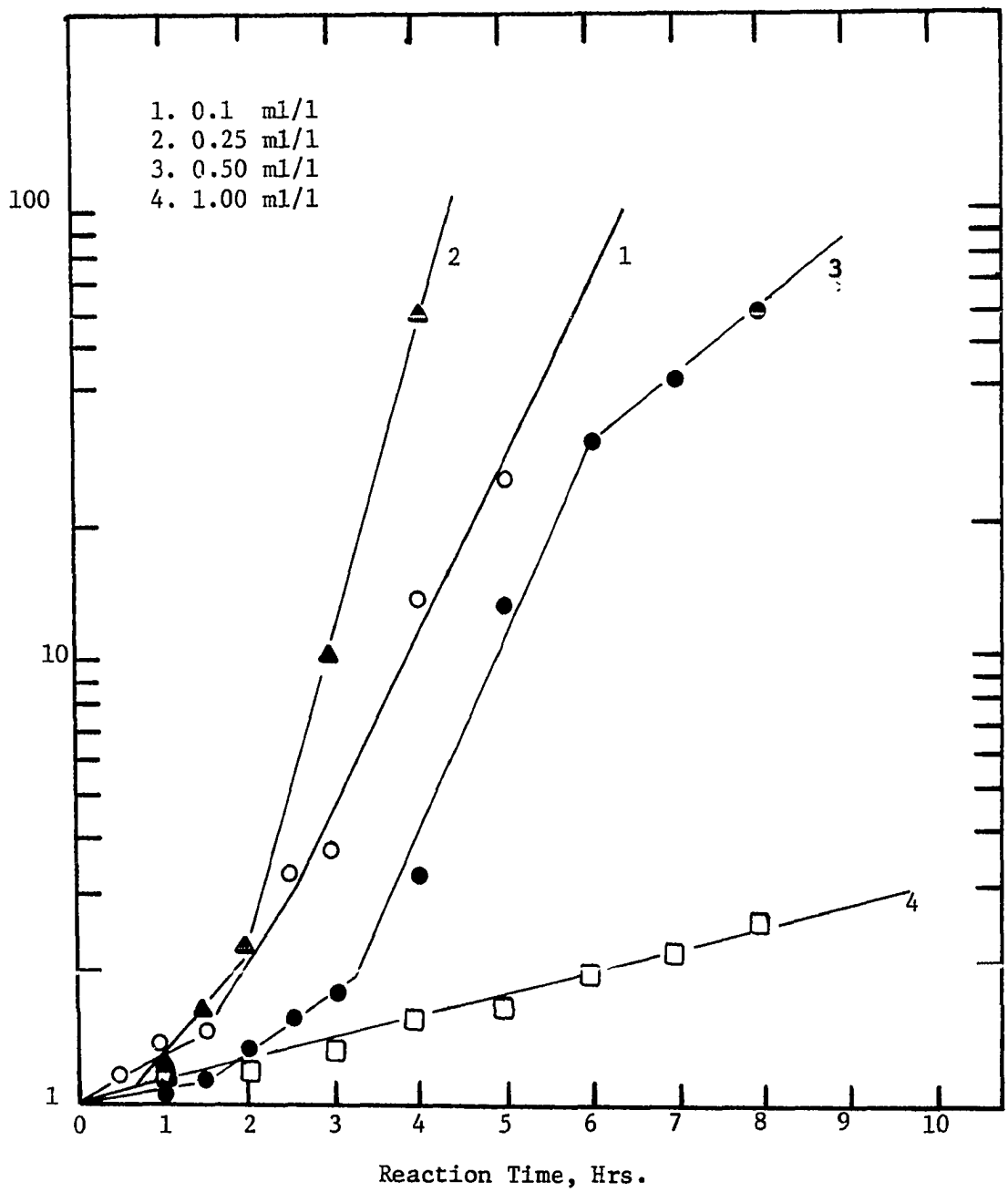


Figure 22. The Effect of Initial Concentration on the Photooxidation of Hexanol in Aqueous Solution.

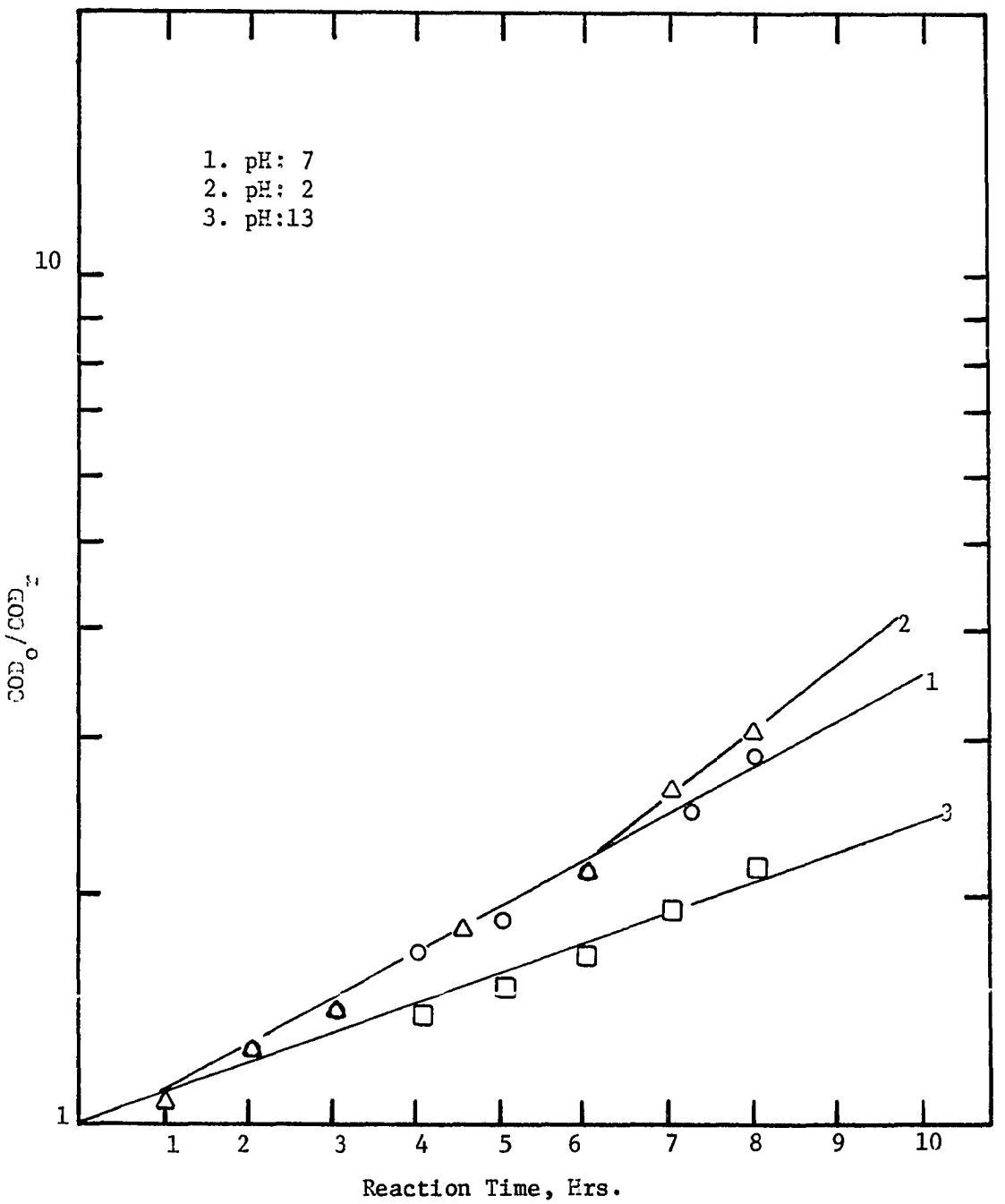


Figure 23. The Effect of pH on the Extent of Direct Photooxidation of Aqueous Solution of Hexanol, 1 ml/1, in Terms of COD Reduction.

not enhance the reaction substantially as it did in the phenol or cyclohexanone solutions. Earlier in the discussion, it was assumed that an acid is the first intermediate in this process. Therefore, if the transformation of the alcohol to the acid is the controlling reaction, then the overall rate will not be particularly affected by other factors that do not increase the rate of acid formation.

The effect of hydroxyl ions on the reaction may be associated with the adverse nature of the alkaline conditions and the formation of a peracid. Recalling the formation reaction of peracid as discussed in literature, it is known that the reaction will occur only in the presence of 1% sulfuric acid. If, in fact, the decomposition of the peracid governs the extent of this reaction, i.e. COD removal, then naturally OH^- will repress the rate of the overall reaction.

Figure 24 illustrates the reaction of phenol, cyclohexanone and hexanol with approximately the same initial concentration expressed in terms of mg/l COD.

Cyclohexanone is readily decomposed and transformed into caproic acid, which in turn undergoes rapid fragmentation that brings about the elimination of the oxidizable organics. Hexanol can be photooxidized and decomposed into smaller fragments by way of the assumed autoxidation or autocatalytic oxidation, its primary process. On the basis of this suggested mechanism the removal of COD of the solution could not be expected to proceed as fast as that of the ketone. The decomposition or oxidation of phenol, involves breaking the aromatic ring which requires more energy. Because of other complicating factors, i.e. deactivation, formation of colored products, the reaction rate measured experimentally must be lower

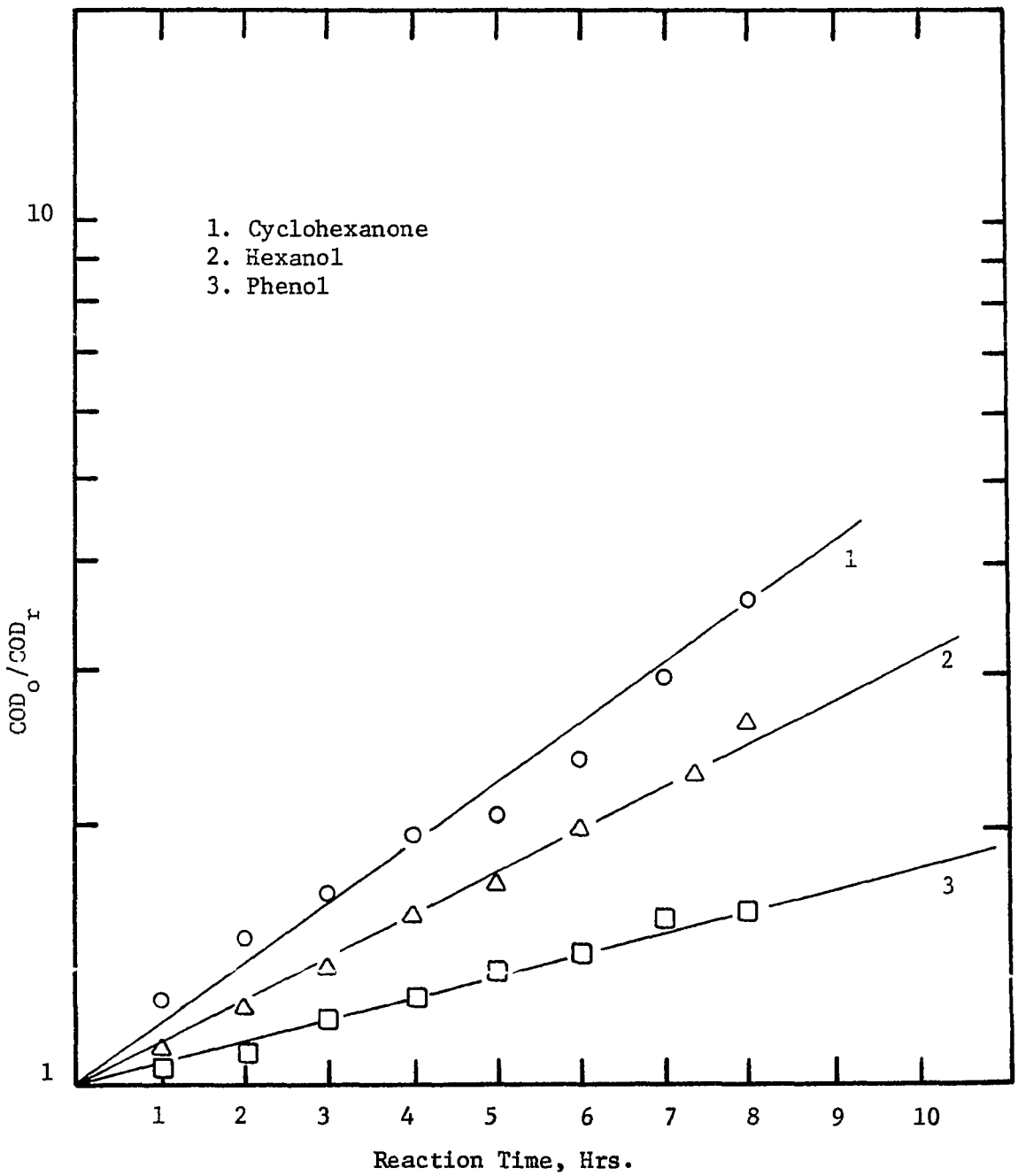


Figure 24. A Direct Photooxidation Comparison of Aqueous Solutions of Hexanol, Cyclohexanone and Phenol.

than that of the other previously mentioned compounds.

Ethyl-Alcohol

The results of the studies on the extent of photodegradation, ZnO sensitized oxidation and direct photooxidation are presented in Figure 25. The reaction kinetics are somewhat similar to that of phenol. Under the experimental conditions applied to the system, note that the photodegradation is very ineffective in transforming or removing the ethanol from the solution. Notice also that one consequence of the oxidation by hydrogen peroxide in the absence of a catalyst is that the rates of conversion and reduction of the oxidizable organic are such that a very long reaction time is required to achieve complete removal. In spite of the fact that ethanol has an absorption peak below 2000 Å, the alcohol undergoes rapid photooxidation, coupled with decomposition. Assuming that the process consists of a series of consecutive reactions, the lag or low k value that appears in the plotting may indicate that the mechanism of the ethanol photooxidation follows the same principle elucidated from the oxidation of hexanol.

Butanol, Isobutanol and t-amyl Alcohol

The extent of direct photooxidation of C_4-C_5 alcohols, as measured by the remaining COD, is illustrated in Figure 26. It points to a conclusion; that the rate of fragmentation or total oxidation of alcohol varies with its chemical structure. The oxidation of n-butanol, 4 carbon atoms, and a branched t-amyl alcohol, 5 carbon atoms, proceeds at about the same rate; whereas, iso-butanol, a secondary alcohol with 4 carbon atoms, indicates higher susceptibility than its corresponding primary alcohol. For the purpose of comparison the hexanol data (C_6) was plotted alongside the

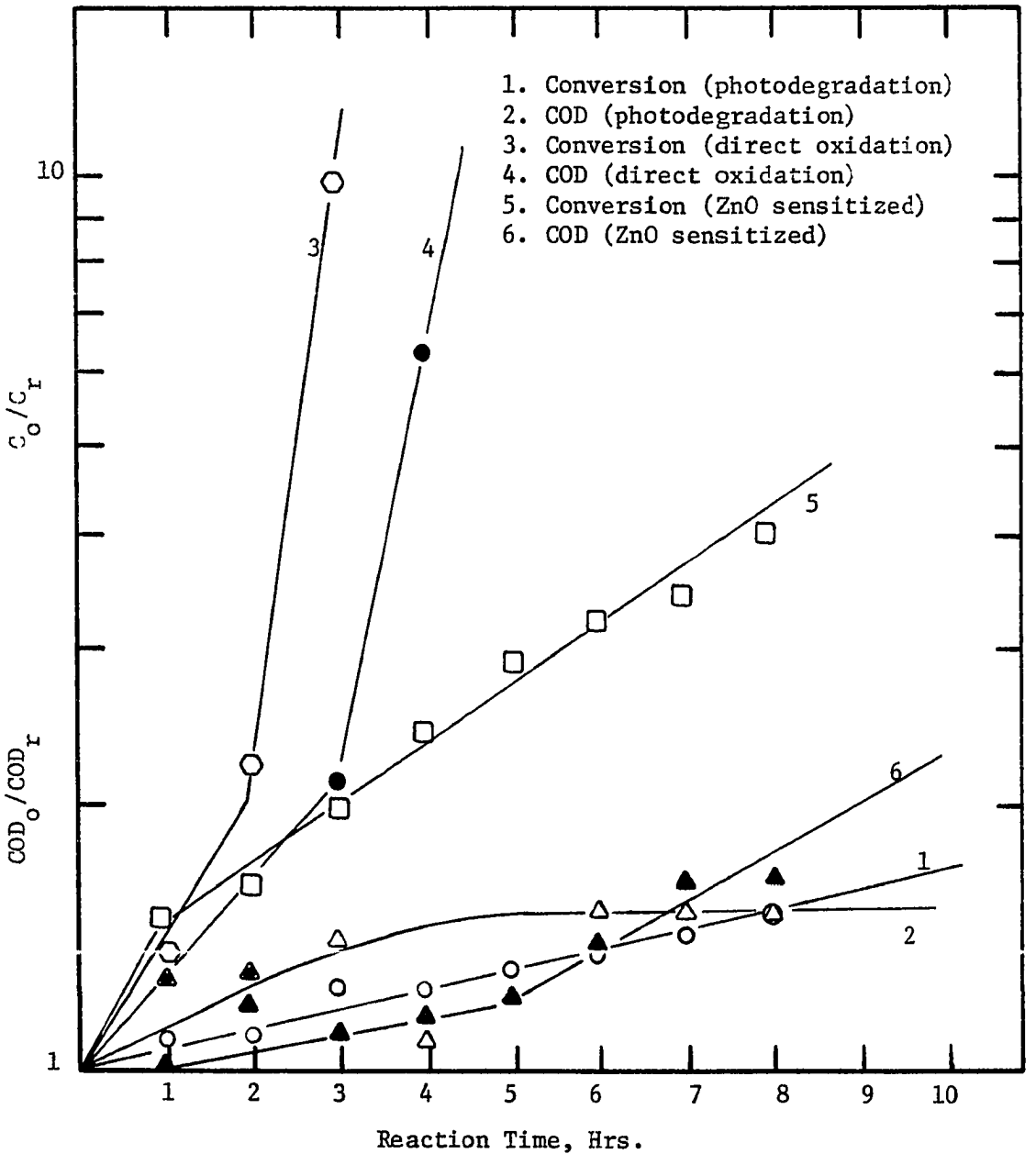


Figure 25. The Extent of Photodegradation, Direct Photooxidation and ZnO Sensitized Oxidation of Ethanol in Aqueous Solution Measured in Terms of COD and Rate of Conversion.

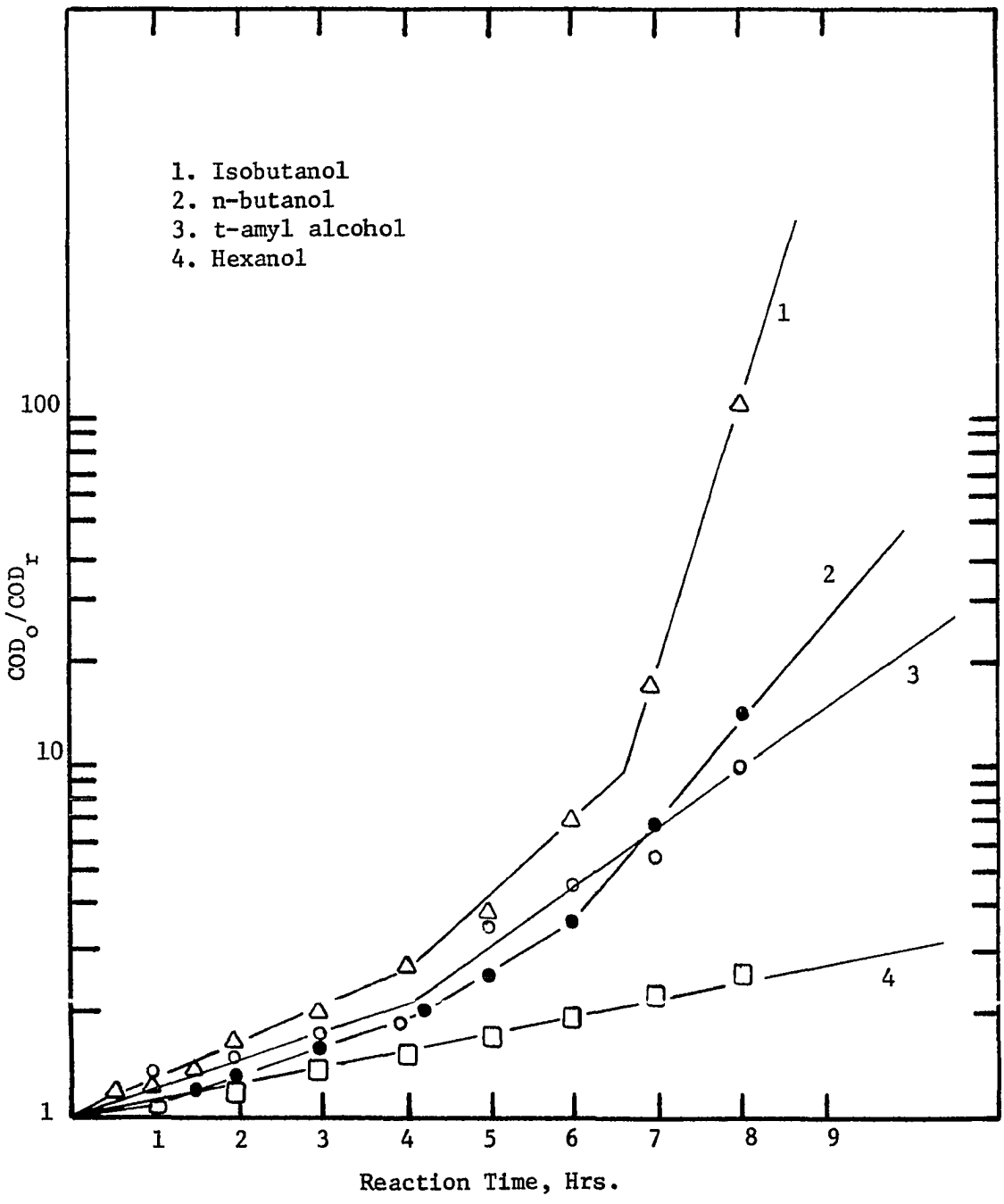


Figure 26. The Extent of Direct Photooxidation of Aqueous Solutions of C_4-C_6 Alcohols.

other three alcohols.

Photooxidation of C_1-C_6 Alcohols and Their Acids

The data obtained from the direct photooxidation of C_1-C_6 alcohols and acids are presented in Figures 27 and 28. The first illustrates the reaction behavior of formic, acetic and propionic acids; whereas, the latter represents reactions modes of the alcohols --all in terms of COD reduction. The inconsistency of the data makes the interpretation difficult and the problem is compounded by the lack of other information. The conclusions presented here are drawn from qualitative evaluations.

1. The removal of COD from an acetic acid solution shows different trends to that of propionic or formic acid. The difference may be cause by the initial acetic acid concentration, which was lower than the concentrations of the other two acids.
2. The change in the reaction rate constant in the oxidation of propionic acid can be related to the oxidation of the products --possibly C_2 oxy-compounds, if the reaction goes via the formation of peracid and is followed by its decomposition. This argumentation is reasonable for propionic acid, but not for formic acid.
3. With the exception of methanol, the results show that for the series C_1-C_6 alcohols, and one derivative of C_{12}, the lower the number of C atoms, the faster the reaction will proceed to completion. Why methanol does not follow this pattern is not understood. It must be pointed out that in all cases a lag or induction-time exists with methanol,

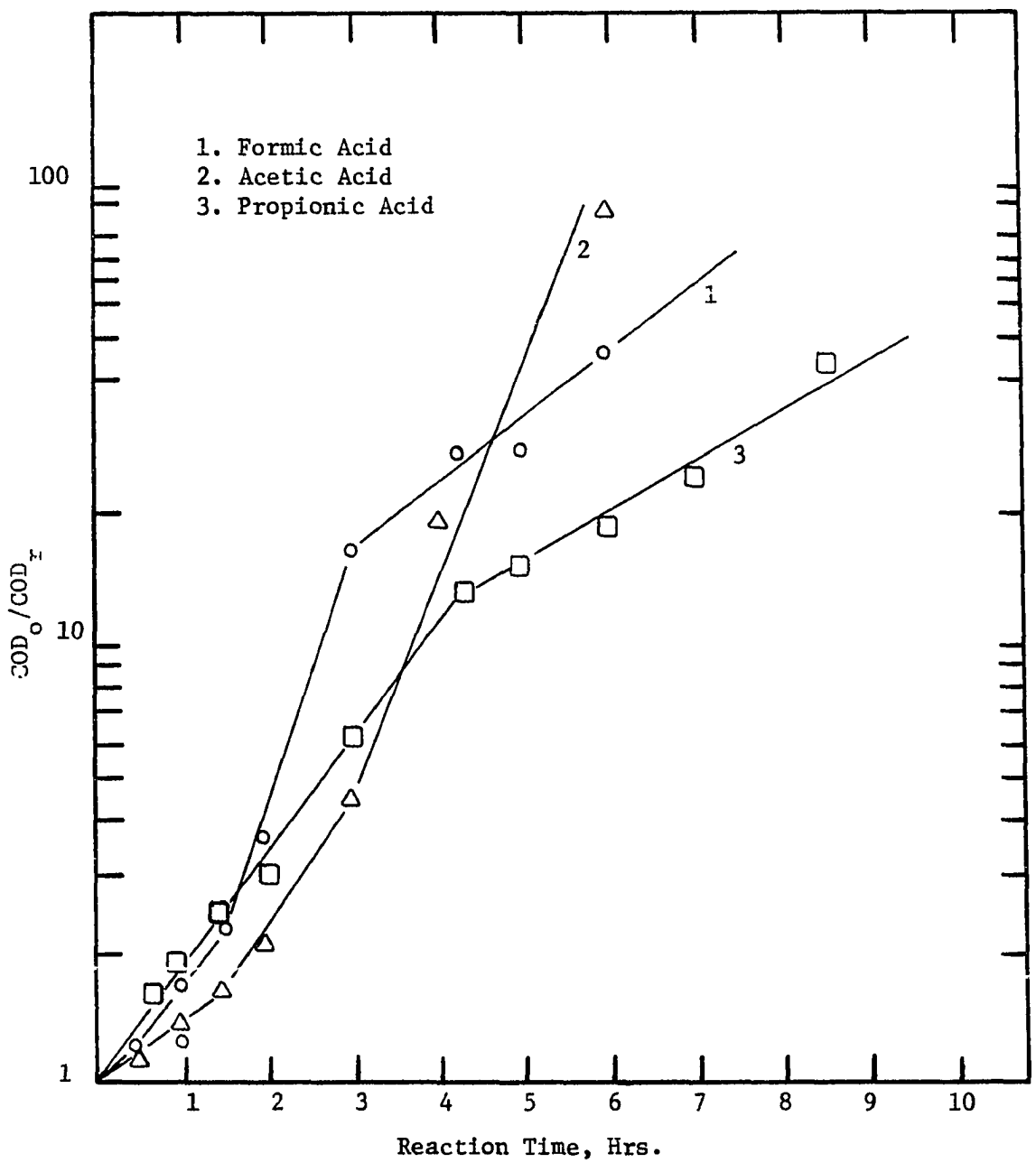


Figure 27. The Extent of Direct Photooxidation of Aqueous Solutions of Organic Acids, C_1-C_3.

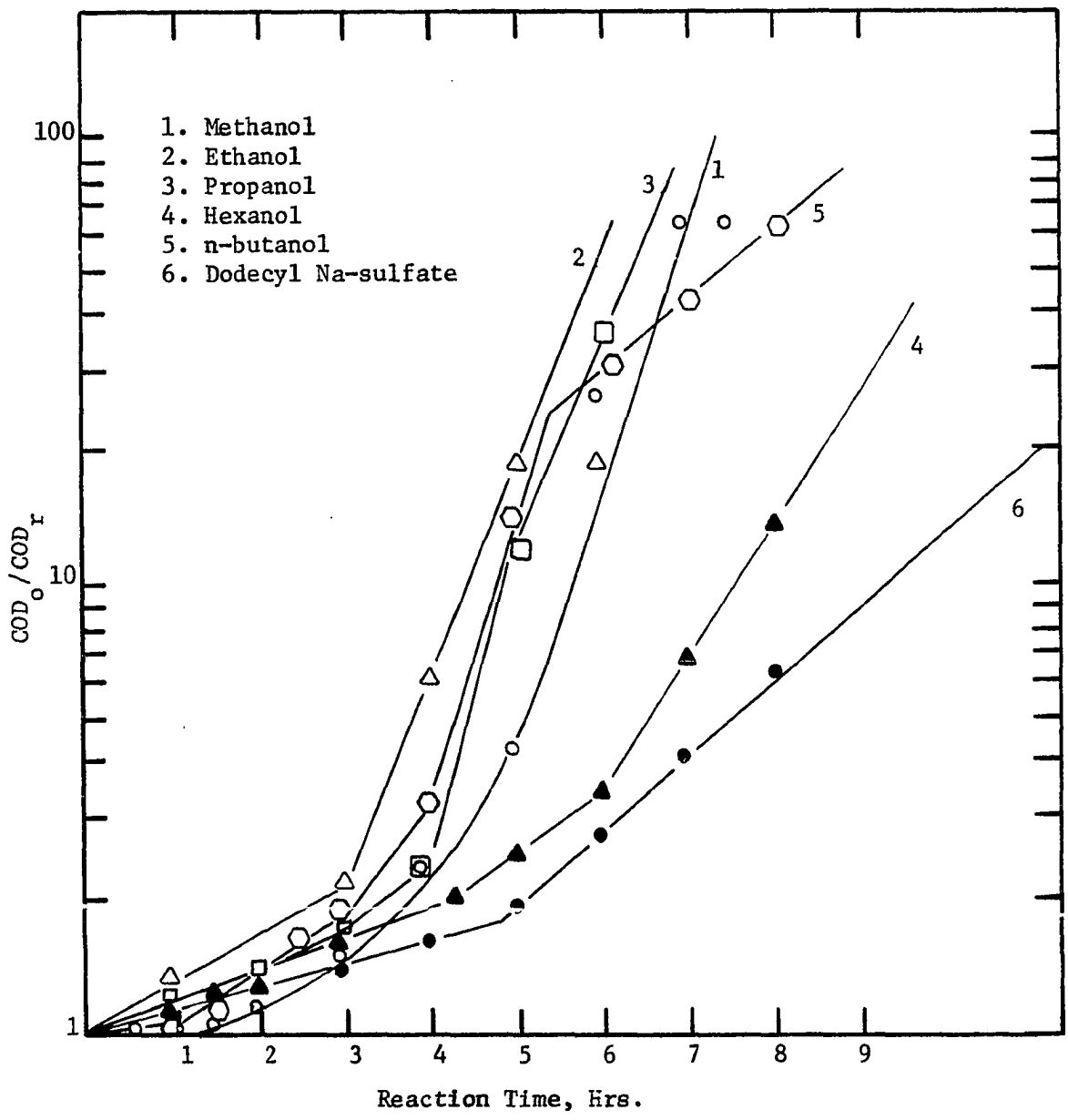


Figure 28. The Extent of Direct Photooxidation of C_1-C_6 Alcohols in Aqueous Solutions.

which is the most significant. Whether this can be correlated to the slowness of the autoxidation that is assumed to be the initial step, is not known.

Photooxidation of Dodecyl Sodium-Sulfate and Socium Stearate

The oxidation of dodecyl Na-sulfate, C_{12}, and Na-stearate, C_{18}, indicates that these compounds are more readily oxidized by direct photo-oxidation than by ZnO sensitized reactions. The results are presented in Figure 29 and the interpretation of the data is analogous to the previous discussion for hexanol and other compounds.

The data obtained from this set of experiments were tabulated in Appendix E, Tables E-2 through E-24.

Final Experiments

Having acquired some basic information pertaining to the nature of the photooxidation process, a set of experiments was performed to explore the applicability of photochemical reactions on some industrial waste constituents. As mentioned earlier, the materials chosen were: vegetable oil (soybean oil), paper pulp and free cyanide. The results and discussion are presented below.

Vegetable Oil

Soybean oil contains a relatively large amount of unsaturated fatty acids, i.e. oleic, linoleic and linolenic. The composition of this oil is:

Total saturated, mainly stearic and palmitic: 11.9-15.8%
Total unsaturated, mainly oleic and linoleic: 88.1-84.2%

Tables F-1 to F-9 of Appendix F summarize the results of the experiments. The change in COD of the irradiated dilute oil emulsion is not

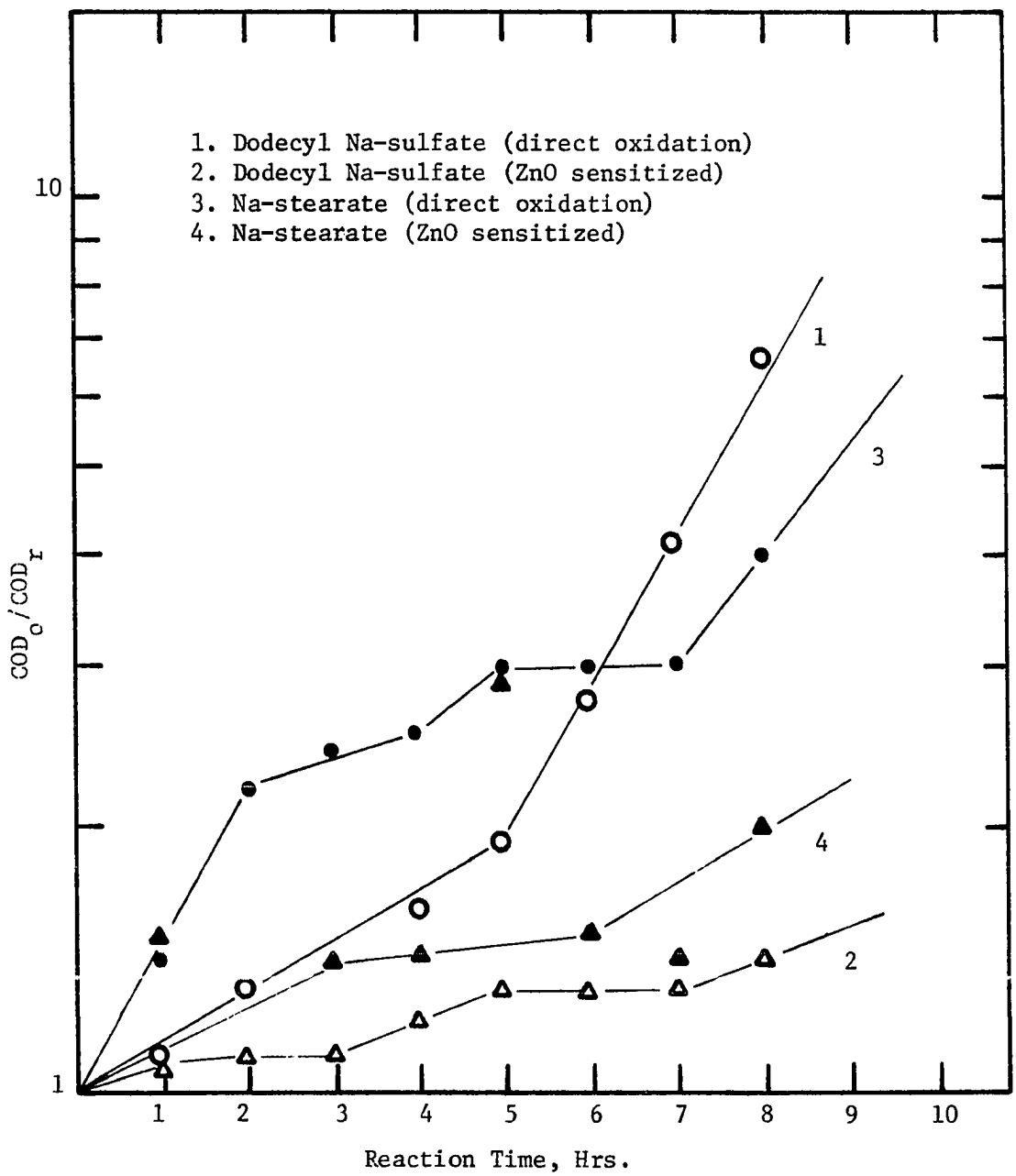


Figure 29. The Extent of Direct Photooxidation and ZnO Sensitized Oxidation of Aqueous Solutions of Dodecyl Na-sulfate and Na-stearate.

consistent. The increase of COD may be due to the photochemical reaction that causes the oil to become more susceptible to dichromate oxidation. The decrease, however, can be due either to the result of fragmentation or the polymerization which was observed. At the end of the experiment, it was found that a considerable amount of sticky material was formed on the wall of the immersion well. Polymerization is likely to occur because of the presence of double bonds in the major constituents of the oil. From this information, it is not possible to state conclusively that the reduction of COD is the result of photofragmentation, or that the removal of the oxidizable organic from the solution is by way of polymerization.

Direct photooxidation of pure linoleic acid (Table F-3, Appendix F) showed that the reduction of COD that could be achieved in 8 hours was relatively low. Similar sticky material was formed on the immersion well. This leads to a tentative conclusion that the decrease in fatty acid concentration is the result of polymerization rather than fragmentation. This may be the mechanism for the reduction of oxidizable organics from oil emulsion.

Paper-Pulp

The results of ZnO photosensitization and direct photooxidation of paper pulp suspension are presented in Tables F-4 and F-5, Appendix F. The data clearly indicates that the outcome of this experiment is inconclusive. The inconsistency is believed to be due primarily to the error in sampling. As the cellulose fibres do not have the same length and it was difficult to keep the suspension in uniform condition, the samples might not be representative of the actual state. Visually, there was no significant change in the suspension appearance; therefore, an insignificant

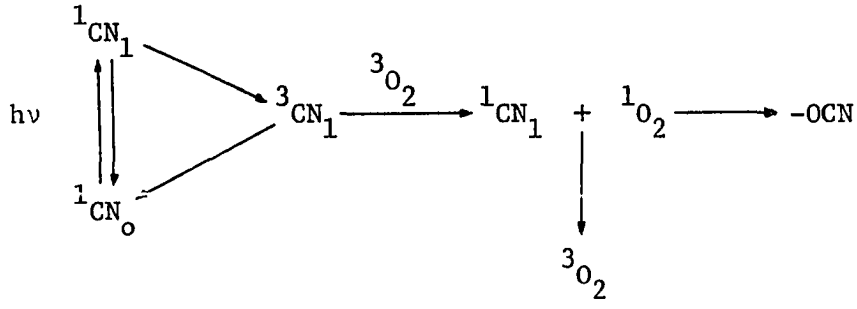
reduction in COD is conceivable.

The condition of the chemical reactor was such that it was impossible to obtain representative samples, and because time did not permit, no further attempts were made to explore the extent of photooxidation of paper pulp.

Free Cyanide

Another interesting application of photochemical reactions is the direct photooxidation of free cyanide in aqueous solution. The experiments were confined to the direct photooxidation and ZnO sensitized oxidation of free cyanide. The results were compiled in Tables F-6 through F-9 of Appendix F.

Free CN^- being singlet in its ground state, has an absorption band below 3880 Å, and is speculated to react quite readily with singlet molecular oxygen. The reaction mechanism for the formation of the first intermediate --possibly -OCN-- is assumed to follow the pathway suggested by Young [17].



Since the analytical method used, silver nitrate titration or colorimetry, detects only free CN^-, the disappearance of the irradiated ions did not necessarily imply that CN^- had been completely oxidized to CO_2 and nitrogen. The rates of reactions, in terms of remaining free cyanide and the effect of the initial concentrations, are shown in Figure 30.

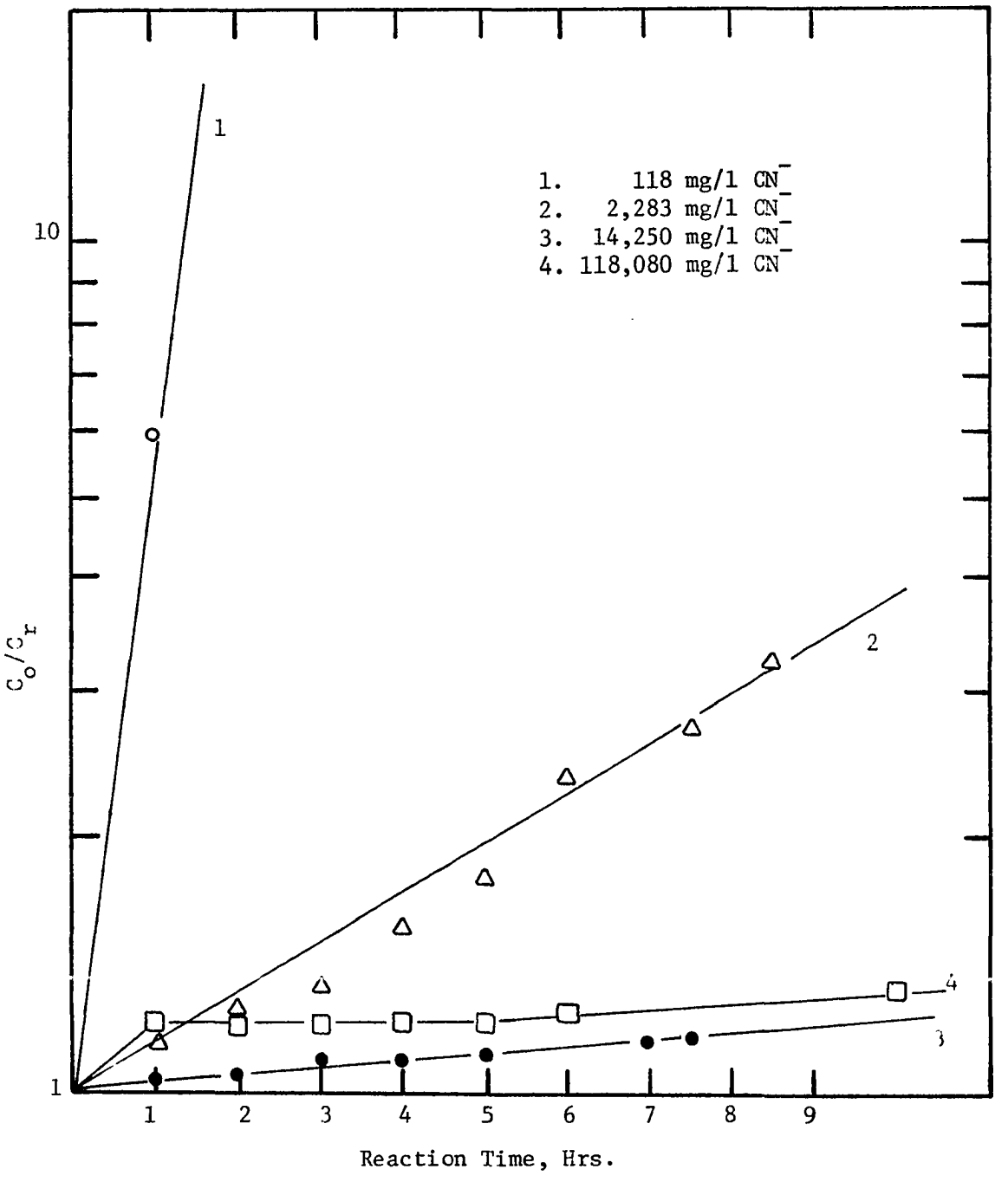


Figure 30. The Effect of Initial Concentration on the Extent of Direct Photooxidation of Free Cyanide in Aqueous Solution.

The reaction is presumably pseudo first order with respect to free CN^- and the concentration quenching process reverses the reaction significantly at a high CN^- concentration.

It is pointed out that because of the high sensitivity of the analytical method used, a high dilution ratio was applied for each titration conducted. Hence, any error involved in the test would be magnified in the final result. This may be the cause of the inconsistency of the data as observed in the plottings, i.e. line representing 100,000 mg/l initial concentration.

The effect of wavelengths on the extent of cyanide oxidation was studied by running a series of experiments using different absorption sleeves. The sleeves used have the following characteristics:

Absorption Sleeve	Thickness, mm	Approximate λ(Å) for % Transmission Indicated		
		50%	30%	100%
Vycor	2	2230	2170	2130
Corex	2	2830	2800	2670
Kimax	2	3270	3200	3090

Table XVIII represents the experimental data and the results indicate conclusively that wavelengths above 2300 Å are not effective in the photo-oxidation of a free cyanide.

Table XIX shows the effect of oxidizing agents used, oxygen vs. air. In the event that singlet molecular oxygen is the major oxidizing species, then the lower efficiency of air in this process can be related to the concentration of excited oxygen present at any one time. Air, containing 21% of oxygen, will produce at most one-fifth of the excited oxygen for

TABLE XVIII

DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE BY PURE OXYGEN AND AIR USING 450 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	Oxygen		Air	
	$CN^-_{remaining}$ mg/l	% Removal	$CN^-_{remaining}$ mg/l	% Removal
0	1176	-	1078	-
1	980	16.7	1078	0
2	737	37.5	980	9.1
3	539	54.2	852	21
4	441	62.5	736	31.7
5	245	79.2	637	40.9
6	49	95.8	539	50
7	49	95.8	442	59.1
8	0	100	392	63.6

TABLE XIX

DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE USING 450 WATT HIGH-PRESSURE LAMP WITH DIFFERENT ABSORPTION SLEEVES AT pH 12

Reaction Time, Hrs.	ABSORPTION SLEEVE							
	None		Vycor		Corex		Kimax	
	CN^-	% rem.	CN^-	% rem.	CN^-	% rem.	CN^-	% rem.
0	1176	-	1176	-	1176	-	1127	-
1	980	16.7	1029	12.5	1176	0	1127	0
2	735	37.5	931	20.8	1176	0	1127	0
3	539	54.6	784	33.3	1176	0	1127	0
4	441	62.5	735	37.5	1176	0	1127	0
5	245	79.2	588	50	1176	0	1127	0
6	49	96	441	62.5	1176	0	1127	0
7	49	96	392	66.7	1176	0	1127	0
8	0	100	342	70.8	1176	0	1127	0

the same flow rate of corresponding gases. In addition, the efficiency of the formation of singlet oxygen will be further affected by the physical/chemical deactivation of the excited state by quenching molecules present in air.

Table XX represents the significance of the energy source applied to the system. For constant physical and chemical conditions, geometry of the reactor, concentration, substrate, etc., it is reasonable to assume that efficiency of the process will only increase proportionally within a certain region, beyond which the energy input must have a diminishing return.

Table XXI shows the results of autoxidation of an aqueous solution on free cyanide. The failure of this process to reduce a measurable amount of the ions manifests the involvement of the excited state CN in the photo-oxidation and the elmination of free cyanide.

The results from the ZnO sensitized oxidation of free cyanide are given in Table XXII. The ineffectiveness of this process to oxidize free cyanide ions can be correlated to show the slowness of hydrogen peroxide oxidation in the absence of a catalyst and at a high pH.

The study of the effect of light on the hypochlorination of free cyanide using sodium hypochlorite solution was also conducted, but the results were inconclusive. Table XXIII represents one set of the experimental data.

Energy Consumption

Based on the data obtained, it would be premature to make any cost estimates for the process. There are several important factors to consider

TABLE XX

EFFECT OF LIGHT SOURCE ON THE DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE

Reaction Time, Hrs.	450 watt lamp		550 watt lamp	
	$CN^-_{remaining}$ mg/1	% Removal	$CN^-_{remaining}$ mg/1	% Removal
0	1176	-	1176	-
1	980	16.7	883	24.9
2	735	37.5	490	58.3
3	539	54.3	142	87.9
4	441	62.5	49	95.8
5	245	69.2	0	100
6	49	95.8		
7	49	95.8		
8	0	100		

TABLE XXI

AUTOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE AT pH 12

Reaction Time, Hrs.	CN^- remaining, mg/l	% Removal
0	2300	-
1½	2300	0
2½	2300	0
3½	2300	0
4½	2300	0
5½	2300	0
6½	2300	0
7	2300	0
8½	2300	0

TABLE XXII

ZnO PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE
CN^-:ZnO = 1:1, USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	$CN^-_{remaining}$, mg/l	% Removal
0	2200	-
2	2200	0
3	2200	0
4	2200	0
5	2200	0
7	2180	0.9
9	2180	0.9

TABLE XXIII

PHOTOINDUCED HYPOCHLORINATION OF AQUEOUS SOLUTION OF FREE CYANIDE
$NaOCl:NaOH:CN^- = 6:6:1$, WEIGHT BASIS, USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	$CN^-_{remaining}$, mg/l	% Removal
0	4160	-
¼	1040	75
1	960	76.9
2	660	84.1
3	600	85.6
4	540	87
5	14	99.7
6	10	99.7
7	6	99.8
8	0	0

Note: By mistake the sodium hypochlorite added was less than the stated ratio.

in estimating the cost of photochemical oxidation on a plant scale. These are:

1. The cost of oxygen;
2. The cost of ultraviolet lamps;
3. The power cost;
4. And the cost of the structure which includes operation cost, i.e. labor, maintainance, interest charges, etc., capital, etc.

The consumption of oxygen is very inefficient, primarily because of its low solubility in water, 9.2 mg/l at 20^{o} C in distilled water, and because the process is generally conducted under atmospheric conditions. In the discussion, it has been pointed out that the overall reaction depends strongly on the rate at which singlet molecular oxygen, or other active oxygen complexes, are formed and on the reactivity of the substrate to the oxidant(s). The lower the reaction rate, the more O_2 will be wasted and the higher the operation cost will be in terms of oxygen consumption, to achieve a certain degree of removal. Air may replace pure oxygen, but quenching of the activated species or singlet molecular oxygen by nitrogen molecules or other quenchers present in air, could reverse the reaction substantially and make the process economically unfeasible.

The cost of the light source can be estimated from the life of the UV lamp. In general, a high-pressure lamp can last for about 1000 hours under good maintanance and operating conditions. Deterioration may be hastened by outside causes, such as improper operating, handling and cleansing. These factors may produce changes which greatly affect the spectral energy distribution, so that the relative intensity of various

portions of the spectrum vary with age.

If the concentration quenching reaction is the major limiting factor on the extent of the reaction, it can then be expected that within a relatively broad time range, the volume of the solution will have less effect on the overall efficiency than will the concentration. It is reasonable to anticipate that the efficiency will be more sensitive to the geometry of the reactor and the degree of mixing, than to the volume of the irradiated solution. On the basis of this consideration, it is deemed improper to estimate the replacement cost of the UV lamp from the available experimental data.

The power requirement can be evaluated from the relationship between the power consumption, to achieve complete oxidation, and the initial concentration of the substrate. Figure 31 depicts this relationship for phenol, hexyl-alcohol and free cyanide.

The slope of the line reflects the sensitivity of power consumption for complete oxidation to the intitial concentration of the irradiated solution. These lines show how some interesting features can be interrelated to the reaction behavior discussed earlier in this chapter.

1. At a phenol concentration range, corresponding to 230 mg/l-1200 mg/l COD, the power consumption increases at a relatively low rate, indicating that the system is not too sensitive to the rise in concentration. However, beyond the upper level of the range, the energy required for complete destruction increases rapidly. This implies that, other conditions being equal, the adverse effect of concentration can be resolved by increasing the output of the

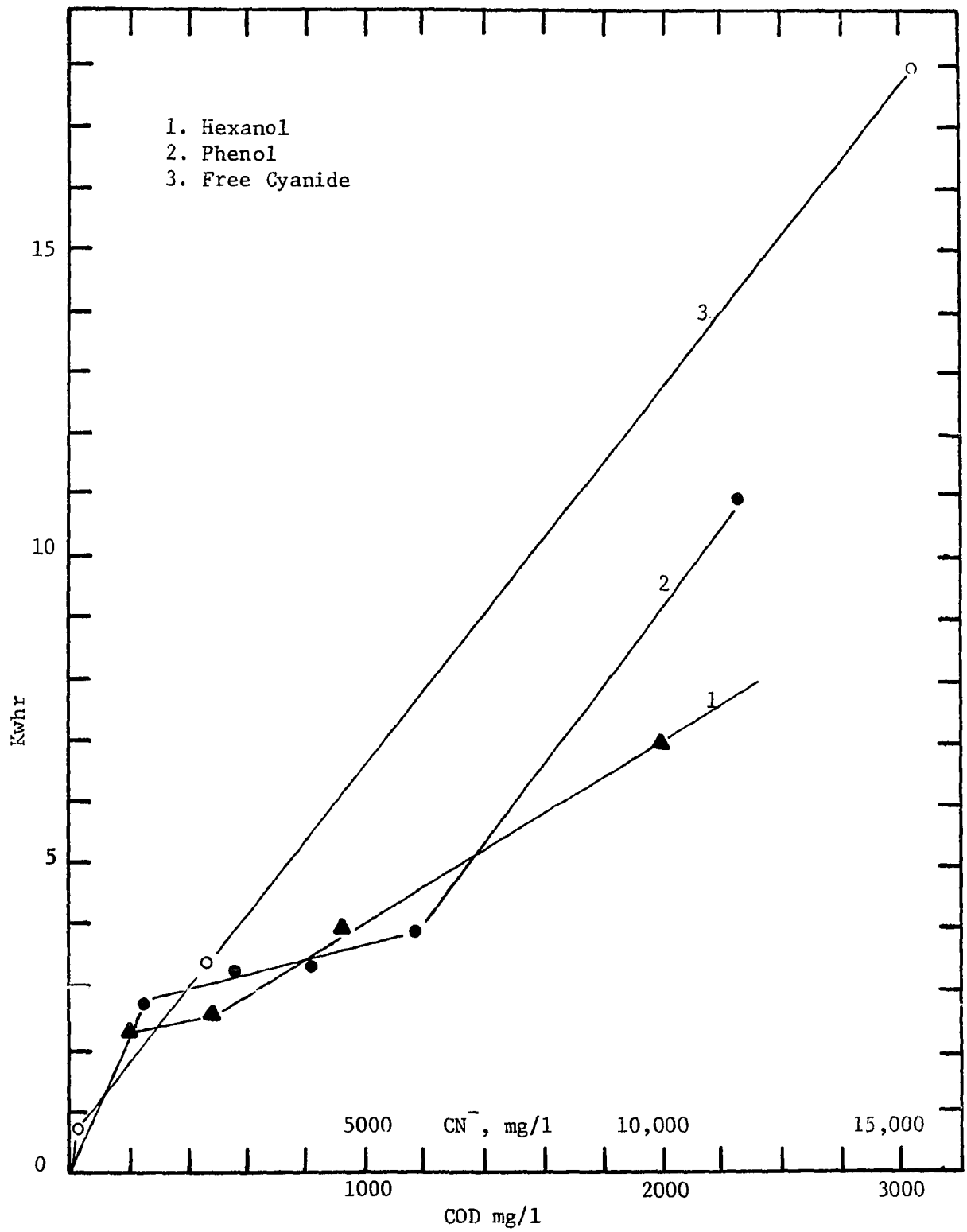


Figure 31. Power Consumption for Complete Photooxidation of Phenol, Hexanol and Free Cyanide as Function of Initial Concentration.

energy lamp source.

2. For hexanol and cyanide, the power consumption increases proportionally with initial concentration. Beyond this initial concentration, equivalent to about 1400 mg/l COD, the increase in the power requirement for hexanol oxidation is substantially less than that for phenol.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This research work is a preliminary attempt to develop a photochemical process applicable to wastewater treatment. Because of the complexities of the reactions involved and the limited amount of time the investigation has been oriented toward acquiring a basic understanding of the fundamentals and disclosing the limitations of the process. On the basis of this experimental approach the following conclusions were drawn:

1. Photodegradation is a relatively simple operation, but its low efficiency makes this process economically and technically unfeasible.

   The adverse effect of high concentrations on the degradation reaction, and the breaking of only one or two bonds, place a constraint on this process. It is only applicable to a highly diluted waste in which the aim is to transform the molecular structure bringing about a reduction of undersirable properties. The destruction of pesticides --solubility ranges from 20-50 micro-grams/liter-- and the reduction in toxicity as the result of irradiation is an example for which this photodegradation process may be effective [7].

2. Dye sensitized oxidation or photodynamic action has been shown to be very efficient for the oxygenation of a large spectrum of organic compounds [6,10,13,14,15,16,17,22,43, 50,51].

   The experimental results of this study, however, indicate that the oxygenation reaction does not necessarily result in reduction of the oxidizable organics, or COD, which primarily interest sanitary engineers. The data show that the conversion efficiency by dye-sensitized photo-oxidation, i.e. the disappearance of the substrate as the result of the reaction, ranges from 0% for Methylene Blue to 46% for Eosin Yellow, and in all cases no significant reduction in COD was observed.

   The study further indicates that dye sensitized photooxidation is only applicable in wastewater treatment if the following conditions are met:

   a. the dye has a very high reactivity to oxygen and will not undergo permanent chemical change under irradiation.
   b. the reaction results in the fragmentation of oxygenated compounds into CO, CO_2 or other gaseous fragments.
   c. the dye molecules are easily attached on particles without being leached out during the process.

3. Pigment sensitized oxidation has a higher efficiency in COD reduction, than dye sensitized photooxidation, but it is a slow process and is therefore economically unfeasible

for wastewater treatment. The slowness of the reaction rate reflects the nature of hydrogen peroxide oxidation, which is generally not rapid enough in the absence of a catalyst and under non-acidic conditions. In spite of this, pigment sensitized oxidation may find importance in natural purification or in understanding the organic cycle of a fresh water system.

Finally, it can be concluded that photosensitized oxidation will be practical if the reaction rate can be increased and the problem of separation of the sensitizer from the system is eliminated. This problem can be resolved by using a solid polymer sensitizer that is placed in a column irradiated by a suitable light source and the aqueous solution is slowly run over the sensitizer. Some work has been done on this heterogeneous photosensitization using solid polymer polyphenyl ketone as the activator.

4. Direct photooxidation is more promising than either photodegradation or photosensitized oxidation. However, this process is subject to various complicating factors that must be fully understood if it is to be developed for wastewater treatment.

One of the complicating factors is the adverse effect of the initial substrate concentration, i.e. the so-called concentration quenching reaction.

Recalling the reaction scheme suggested by Young, et. al. [17], it

is conceivable that at least two reactions will determine the efficiency of the process. These reactions are:

1. The formation of a triplet state of substrate A from its singlet excited state.
2. The triplet-triplet energy transfer in the formation of singlet molecular oxygen.

As discussed earlier in Chapter II, at high substrate concentrations the rate of formation of the oxygenated products was determined by the rate of formation of the triplet of the substrate, but this triplet will in turn decay proportionally with the concentration of the substrate and oxygen concentration.

The relationship discussed implies that there is a critical condition where the rate of the formation of the triplet state is equal to its decay rate. At a constant oxygen concentration, the substrate will then be the limiting factor that determines the critical condition.

Now consider the energy transfer given by the equation:

$$^3A_1(\text{donor}) + {}^3O_2(\text{acceptor}) \longrightarrow {}^1A_1 + {}^1O_2$$

In order that the energy transfer process between donor, $^3A_1$, and acceptor, $^3O_2$, molecules can occur, there must be an interaction between the triplet state substrate and ground state oxygen.

The mechanisms involved in this energy transfer are the collisional and resonance excitation transfer [35,47]. The first one is diffusion controlled and therefore, physical mixing will play an important role in this energy transfer process. The latter one can take place over distances, R's, much greater than collisional diameter and would not be expected to be associated with diffusion or direct encounter. It is theoretically

established that the rate constant of energy transfer by this mechanism is a function of R^{-6}. There exists a critical distance, R_o, at which the activation and energy transfer are equally probable.

This theoretical consideration supports the findings that the rate of photooxidation is dependent on the concentration of the substrate. Increasing the concentration of substrate, or oxygen, will decrease the distance, R, and increase the bimolecular rate constant for the energy transfer process. But, the higher the substrate concentration the more significant will be the deactivation of the triplet state. This leads to the conclusion that an optimum condition exists in which the process has a maximum efficiency.

Another complicating factor, that is not explicitily indicated in the reaction scheme, is the nature of the subsequent photooxidation of the product, AO_2. These reactions may or may not follow a similar route by which the first reaction product undergoes oxidation. In the event that the first oxygenated product is a peroxide or a hydroperoxide, then the compound can undergo thermal decomposition, other dark reactions, or it may enter into another oxidation step. Because of this, the order of the reaction is very difficult to determine and therefore, the overall reaction rate constant can only be estimated.

In Type-II photooxidation [14,15,17] the reactions involve only the electronically excited states. Contrary to this in direct photooxidation processes, it is necessary to include the radical formation and possible chain reactions. Therefore, kinetically the process has become so complicated that unless simplifications and assumptions are made, the formulation of the rate equation is virtually impossible.

The effect of geometry, optical thickness or reactor design has been discussed quite extensively in Chapter II. For the formulation of the reactor equations, simplified reaction conditions must be imposed on the system. However, some of these conditions cannot be applied to the reactor equation for direct photooxidation processes used in wastewater treatment. The conditions that must be modified are:

1. That the light is polychromatic. For complete photooxidation, coupled with decomposition of the intermediate oxygenated products into smaller fragments, the use of monochromatic light will not be effective because only the chemical that absorbs the applied wavelength can undergo photochemical reaction. This is due to the fact that with a continuous change in composition and form of the organics, the compound that absorbs the applied wavelength and undergoes photochemical reaction consist of only a small fraction of the total organics. In addition, the insertion of a monochromator to produce a narrow wavelength band reduces the intensity of the transmitted light resulting in severe limitations in reactor size and geometry. Therefore, for engineering applications, polychromatic light is considerably more versatile than the monochromatic light even though monochromatic light is more selective for a particular reaction.
2. The composition of the irradiated solution changes continuously during the process and the overall extinction coefficient and molal absorptivity will vary accordingly.

3. The possibility of dark reactions occurring.
4. As presented earlier in the discussions of the experimental results, the overall reaction, in terms of COD removal, is neither pseudo-first order or second order with respect to the oxidizable organic. However, the rate of conversion or disappearance of the substrate is first order with respect to the same reactant.

Finally, considering the established theory of photochemical oxidation in aqueous systems and the data obtained from the experiments performed to date, it is reasonable to conclude that due to the process constraints the application of photooxidation in wastewater can only be made on a selective basis. Once the method has been selected, the performance of the process has to be evaluated from a "black-box" approach. This implies that the detailed chemical aspects, such as mechanisms, forms of the intermediates, etc., are not of great interest from water pollution abatement points of view. It is the quality of the final effluent that is of major concern to the environmental scientists. The data indicate that depending on the nature and concentration of the substrate the COD removal was 90% in 120 minutes for phenol (initial concentration 100 mg/l) and 99% in 60 minutes for free CN^- and formic acid (initial concentration 120 mg/l and 245 mg/l, respectively).

Based on the experimental results reported here and considerations of the fundamental theory of photochemical processes, it is felt that direct photooxidation in aqueous solutions is applicable to the treatment of organic wastes with total organic carbon concentrations of less than 100 ppm, and for advanced waste treatment or polishing processes aiming

at the total destruction of the refractory or undesirable materials.

As discussed in the previous chapter, the present knowledge of the process has been such that any attempt to make cost estimation from this study is considered premature. This is justifiable if the following facts are considered:

1. The processes discussed were not conducted under optimum conditions. Therefore, a cost estimation based on these inefficient conditions would result in an inordinately high cost.
2. To obtain a realistic operation cost, a scale-up of the process should be performed. Unfortunately, there are several parameters that cannot be estimated from the existing experimental data. These are:
   a. efficiency of oxygen consumption;
   b. effect of reactor volume to light absorption efficiency;
   c. geometry of the reactor (parallel, cylindrical or annular).

It is possible, however, to predict roughly the order of magnitude of the process cost to photooxidize an organic bearing waste. The cost estimate is based on similar studies performed by Bulla and Edgerley [7] and Meiner et. al. [32].

According to Bulla and Edgerley [7] the extrapolated operation cost for 99% photodecomposition of pesticides will range from 16¢ to 49¢ per 1000 gallons. Meiner [32] estimated an operation cost of 7¢ to 11¢ per 1000 gallons for the UV light induced chlorination of a 10 mgd plant

treating highly nitrified effluent containing 30 mg/l COD.

Now, considering the low efficiency of photodegradation process on one hand and taking into account the price of chlorine gas and the low pH at which the reaction is effective on the other, the following estimate can be made. Photooxidation, being more effective than photodegradation but less rapid than photo-induced chlorination, is predicted to operate with a cost in the range of 12¢ to 48¢ per 1000 gallons. This estimation indicates that direct photooxidation is less expensive than γ-irradiation processes which are reported to operate at $1.10/1000 gallons to treat a waste containing 100 ppm pollutant.

Recommendations

The conclusions presented above, suggest that the development and application of a photooxidation process in wastewater treatment, require further indepth investigations focused on the reactor design. The knowledge of photooxidation reaction in aqueous systems is not well established. Hence, the formulation of the process can only be done through experimental procedures. Within this experimental framework, the future studies should include the following aspects:

1. Correlation of the formation reaction of the triplet state of a substrate, with the energy transfer process of the formation of singlet molecular oxygen. Optimization of these two processes is essential for the formulation of the reactor equations. To achieve this goal it is necessary to measure quantum yield of the intersystem crossing process,

$$^1A_1 \longrightarrow {}^3A_1$$

and the bimolecular rate constant of energy transfer:

$$^3A_1 + {}^3O_2 \longrightarrow {}^1A_1 + {}^1O_2$$

Some of the important variables in these process will be the oxygen concentration, degree of mixing and substrate concentration.

2. The complexities of the process have been enormous. This makes it very difficult to determine the order of the reaction and the corresponding reaction rate constant. This problem has to be resolved by determining the range of k values and using these in the derivation of the reactor equation.

3. The concentration quenching reaction has become a constraint in the application of the process for treating concentrated wastes. To cope with this problem there are two possible methods of approach, namely:
   a. improving the efficiency of the process by recycling the irradiated effluent;
   b. restricting the application of the process to dilute solutions containing 10^{-5} - 10^{-4} mole/liter substrates.

   Regardless of the option taken, the study as mentioned in 1. should be performed in advance.

4. The application of polychromatic light necessitates the modification of the approach to formulate the reactor equation. Two factors must be considered when

polychromatic light is used:

a. a method of evaluating the absorption of polychromatic light;

b. and the effect of wavelength distribution to the reaction rate.

For the first problem the experimental data necessary are the emission spectra of the lamp and the attentuation coefficients, which are a function of wavelength for all the chemical species present. The average attenuation coefficient can be estimated from the equation,

$$\bar{\mu} = \frac{\int_{\lambda_1}^{\lambda_2} \mu_\lambda \, I_{w,\lambda} \, d\lambda}{\int_{\lambda_1}^{\lambda_2} I_{w,\lambda} \, d\lambda}$$

where λ_1 and λ_2 are the limits of absorption, and/or the radiation of the lamp.

To account for the variation of kinetic constants with λ, the appraoch to be taken is to evaluate the fraction of the total radiation of the lamp associated with each increment of wavelength, $\Delta\lambda$. Then, Lambert's law given by the equation,

$$\nabla \cdot I = -\mu \, |I|$$

can be applied for each $\Delta\lambda$ using the appropriate μ and I_w. The results so obtained can be used directly in the rate reaction term of the mass balance equation.

Other photochemical processes worth studying with respect to their application and feasibility in wastewater treatment include photo-induced chlorination and heterogenuous oxidation. With respect to photo-induced

chlorination investigations shall be oriented toward obtaining optimum conditions for complete destruction of organic bearing wastes containing refractories such as lignin and its derivatives, i.e. cellulose, etc. or transforming the concerned constituents so that they have higher response to bacterial growth than the original compounds. Regardless of the objective chosen, it is deemed necessary to understand some of the basic reaction mechanisms involved in order that the formation of undersirable reaction product(s) can be avoided, and the process modified.

Another photochemical process that merits investigation is the heterogeneous oxidation, using a solid polymer sensitizer packed in a column irradiated by a suitable light source. A polymer sensitizer with a triplet energy above 50 Kcal/mole and high reactivity to oxygen has to be used. The solid polymer sensitizer can be replaced by an oxygen reactive dye sensitizer impregnated in a transparent inert material.

Because of the high selectivity and specificity of the photosensitized oxidation, this process lacks versatility. The main interest in this investigation stems from the possible use of light in the visible range.

BIBLIOGRAPHY

1. Alexander, M. "Biodegradation Problem of Molecular Recalcitrance and Microbial Fallibility." Advances in Applied Microbiology, Vol. 7, Edited by Umbreit, W.W., New York: Academic Press, 1965.

2. Allen, E.R., Cadle, R.D. "A Study of the Effect of Molecular Oxygen on Atomic Oxygen-Hydrocarbon Reaction." Photochemistry and Photobiology, Vol. IV No. 6, Pergamon Press, (December, 1965), p. 979

3. Bamford, C.H., Wyane, R.P. "Photochemistry in the Liquid Phase." Photochemistry and Reaction Kinetics, Cambridge University Press, 1967.

4. Bishop, D.F., et. al. "Hydrogen Peroxide Catalytic Oxidation of Refractory Organics in Municipal Waste Waters." Industrial and Engineering Chemistry, Process Design and Development, Vol. 7, (January, 1968), p. 110.

5. Boudart, M. Kinetics of Chemical Processes, Englewood Clifs, New Jersey: Prentice-Hall, Inc., 1968.

6. Bourdon, J., Schnuriger, B. "Photosensitization of Chemical Reaction in Organic Solids." Physics and Chemistry of the Organic Solid State, Vol. III, New York: Interscience Publishing Company, 1967.

7. Bulla, C.D., Edgerly, T., Jr. "Photochemical Degradation of Refractory Organic Compounds." Journal of Water Pollution Control Federation, XXXX, (April, 1968), p. 546.

8. Calvert, J.G., Pitts, J.N. Photochemistry, New York: John Wiley and Sons, 1967.

9. Cassano, A.E., et. al. "Photochemical Reactor Engineering." Industrial and Engineering Chemistry, Vol. 59 No. 1 (January, 1967), p. 18.

10. Chambers, R.W., Kearns, D.R. "Triplet States of Some Common Photosensitizing Dyes." Research Note, Photochemistry and Photobiology, Vol. X No. 3, (September, 1969), p. 215.

11. Chari, C.N., Qureshi, M. "Photochemical Formation of Hydrogen Peroxide from Water; Part I, In Presence of Zinc Oxide." Journal Indian Chemical Society, Vol. 21, (1944), p. 97.

12. Davis, A.G. Organic Peroxides, London:Butterworth, 1961.

13. Foote, C.S. "Photosensitized Oxygenation and the Role of Singlet Oxygen." Account of Chemical Research, Vol. 1, (April, 1968), p. 104.

14. Gollnick, K. "Type-II Photooxygenation Reaction in Solutions." Advances in Photochemistry Vol. VI, Edited by Noyes, W.A., Jr., Hammond, G.S. and Pitts, J.N., New York: John Wiley and Sons, 1967.

15. Gould, R.F. Oxidation of Organic Compounds III, Advances in Chemistry Series, Washington, D.C.: American Chemical Society, 1968.

16. Grossweiner, L.I. "Molecular Mechanisms in Photodynamic Action." Photochemistry and Photobiology, Vol. 10 No. 3, (September, 1969), p. 183.

17. "International Conference on Singlet Molecular Oxygen and Its Role in Environmental Sciences." Annals of the New York Academy of Sciences, Vol. 171 Article 1, (October, 1970).

18. Irvin, R.L., Bush, A.W. "Factors Responsible for Non-biodegradability of Industrial Waste." Journal of Water Pollution Control Federation, Research Supplement Vol 41 No. 11, (November, 1969), p. R 482.

19. Kan, R.O. Organic Photochemistry, New York: McGraw-Hill, 1966.

20. Kashe, V., Lindqvist, L. "Reactions Between the Triplet State of Fluorescein and Oxygen." Journal of Physical Chemistry, Vol. 68, (April 1964), p. 817.

21. Khan, A.U. "Singlet Molecular Oxygen from Superoxide Anion and Sensitized Flourescence of Organic Molecules." Science, Vol. 168 (April, 1970), p. 476.

22. Khan, A.U., Kearns, R.D. "Sensitized Photooxygenation Reaction and the Role of Singlet Oxygen." Photochemistry and Photobiology, Vol. 10 No. 3, (September, 1969), p. 193.

23. Kinney, C.L., Ivanuski, V.R. "Photolysis Mechanism for Pollution Abatement." Robert A. Taft Water Research Center, Report No. TWRC-13, (October, 1969).

24. Knorre, D.G. "Some Elementary Stages in the Liquid Phase Oxidation of Hydrocarbons." The Oxidation of Hydrocarbon in the Liquid Phase, Edited by Emanuel, N.M., New York: Pergamon Press, 1965.

25. Leermakers, P.A., James, F.C. "Heterogeneous Photosensitization" Journal of Organic Chemistry, Vol. 32, (September, 1967), p. 2898.

26. Livingston, R. "Photochemical Autoxidation." Antioxidation and Autoxidation, Vol. I, Edited by Lundberg, W.O. New York: Interscience Publisher, 1961.

27. Littlewood, A.B. Gas Chromatography, Principles, Techniques and Applications, Second Edition, New York: Academic Press, 1970.

28. Lundeon, G., Livingston, R. "Chemiluminescence of Hydrocarbon Oxidation." Photochemistry and Photobiology, Vol. 4 No. 6, (December, 1965), p. 1085.

29. Maizus, Z.K. "The Role of Peroxide in the Liquid Phase Oxidation of Hydrocarbons." The Oxidation of Hydrocarbons in the Liquid Phase, Edited by Emanuel, N.M., New York: Pergamon Press, 1965.

30. Malaney, G.W., Gerhold, R.M. "Structural Determination in the Oxidation of Aliphatic Compounds by Activated Sludge." Journal of Water Pollution Control Federation, Research Supplement, Vol. 41 Part 2, (February, 1969), p. R 18.

31. Markham, M.C., Laidler, K.J. "A Kinetic of Photo-oxidation on the Surface of Zinc-Oxide in Aqueous Suspension." Journal of Physical Chemistry, Vol. 57 (March, 1953), p. 363.

32. Meiner, A.F., et. al. "An Investigation of Light-Catalyzed Chlorine Oxidation for Treatment of Waste Water," Report No. TWRC-3, Robert A. Taft Water Research Center, December, 1968.

33. Miller, L.L., Narang, R.S. "Induced Photolysis of D.D.T." Science, Vol. 169, (July, 1970), p. 476.

34. Moelwyn-Hughes, E.A. Physical Chemistry, First Edition, New York: Pergamon Press, 1957.

35. Owen, E.D. "Principles of Photochemical Reactions in Aqueous Solution" Organic Compounds in Aquatic Environments, Edited by Faust, Samuel J. and Hunter, Joseph V., New York: Marcel Dekker Inc., 1971.

36. Pitts, J.N. "The Vocabulary of Photochemistry." Advances in Photochemistry, Vol. I, New York: John Wiley and Sons, 1961.

37. Pitts, J.N. "Photochemical Air Pollution, Singlet Molecular Oxygen as an Environment Oxidant." Advances in Environmental Sciences, Vol. I, New York: Wiley-Interscience, 1969.

38. Prather, B.F. "Advanced Treatment of Petroleum Refinery Wastewater by Autoxidation." Journal of Water Pollution Control Federation, Vol. 42, (April, 1970), p. 596.

39. Pryor, W.A. Free Radicals, New York: McGraw-Hill, 1966.

40. Rogers, J.H. "The Dissimilation of High Molecular Weight Substances." The Bacteria, A Treatise on Structure and Function, Vol. II, Metabolism, Edited by Gunsalus, I.C. and Stanier, R.Y., New York: Academic Press, 1961, p. 257.

41. Rosenberg, J.L., Humpries, F.C. "The Participation of Excited Oxygen in a Chemiluminescent Reaction." Photochemistry and Photobiology, Vol. 4 No. 3, (December, 1965), p. 1185.

42. Shlyapintokh, V., Emanuel, N.M. "Mechanism of the Photosensitization of the Liquid Phase Oxidation of 2,7, Dimethyl Octane with Molecular Oxygen." The Oxidation of Hydrocarbons in the Liquid Phase, Edited by Emanuel, N.M., New York: Pergamon Press, 1965.

43. Spikes, J.D., Straight, R. "Sensitized Photochemical Processes in Biological System." Annual Review of Physical Chemistry, Vol. 18, Edited by Eyring, H., Christensen, C.J. and Johnston, H.S., Palo Alto: Annual Review Inc., 1967.

44. Stauff, J. "Chemiluminescence of Some Reaction with Molecular Oxygen." Photochemistry and Photobiology, Vol. 4 No. 3, (December, 1965), p. 1199.

45. "Standard Methods for the Examination of Water and Wastewater", 13th Edition, American Public Health Association, New York, 1971.

46. Swisher, R.D. Surfactant Biodegradation, New York: Marcel Dekker Inc., 1970.

47. Turro, N.J. Molecular Photochemistry, New York: Benjamin, W.A., 1965.

48. U.S. Department of the Interior, Federal Water Pollution Control Administration:"A New Ara for America's Water." Publication No. CWA-1, Reprinted March, 1967.

49. "Water Resources Research Catalog." Vol. 6, Part I, U.S. Department of the Interior, Office of Water Resources Research, Washington, D.C., Water Resources Scientific Information Center, December, 1970.

50. Wayne, R.P. "Singlet Molecular Oxygen." Advances in Photochemistry, Vol. 7, Edited by Noyes, W.A., Jr., Hammond G.S., and Pitts, J.N., New York: Interscience Publishing Co., 1969.

51. Zwicker, E.F., Grossweiner, L.I. "Transient Measurement of Photochemical Processes in Dye; The Mechanism of the Photosensitized Oxidation of Aqueous Phenol by Eosin." Journal of Physical Chemistry, Vol. 67, (March, 1963), p. 549.

APPENDIX A

SPECTRAL ENERGY DISTRIBUTION

TABLE A-1

SPECTRAL ENERGY DISTRIBUTION FOR HANOVIA HIGH-PRESSURE QUARTZ MERCUTY-VAPOR LAMPS

Lamp watts	450.0	550.0
Lamp volts	135.0	145.0
Current, amps.	3.6	4.4

Mercury Lines (Angstroms)	Radiated Energy in Watts	
13673(infrared)	2.6	4.6
11287	3.3	3.8
10140	10.5	12.2
5780(yellow)	20.0	23.0
5461(green)	24.5	28.2
4358(blue)	20.2	23.3
4045(violet)	11.0	12.7
3660(UV)	25.6	30.1
3341	2.4	2.8
3130	13.2	15.0
3025	7.2	8.2
2067	4.3	5.0
2894	1.6	1.8
2804	2.4	2.8
2753	0.7	0.8
2700	1.0	1.2
2652	4.0	4.6
2571	1.5	1.8
2537(reversed*)	5.8	5.0
2482	2.3	2.6
2400	1.9	2.2
2380	2.3	2.6
2360	2.3	1.8
2320	1.5	2.4
2224	3.7	4.2
Total Watts	175.8	202.7

*2537 line is reversed in high-pressure lamps.

APPENDIX B

COMPOSITION OF ARTIFICIAL SEWAGE

APPENDIX B

TABLE B-1

COMPOSITION OF ARTIFICIAL SEWAGE

Chemical	mg/l
Dextrose	75.4
Nutrient Broth	48
NH_4Cl	15
NaCl	28
K_2HPO_4	50.8
$MgSO_4$	8

APPENDIX C

PHOTOCHEMICAL REACTOR DIAGRAM

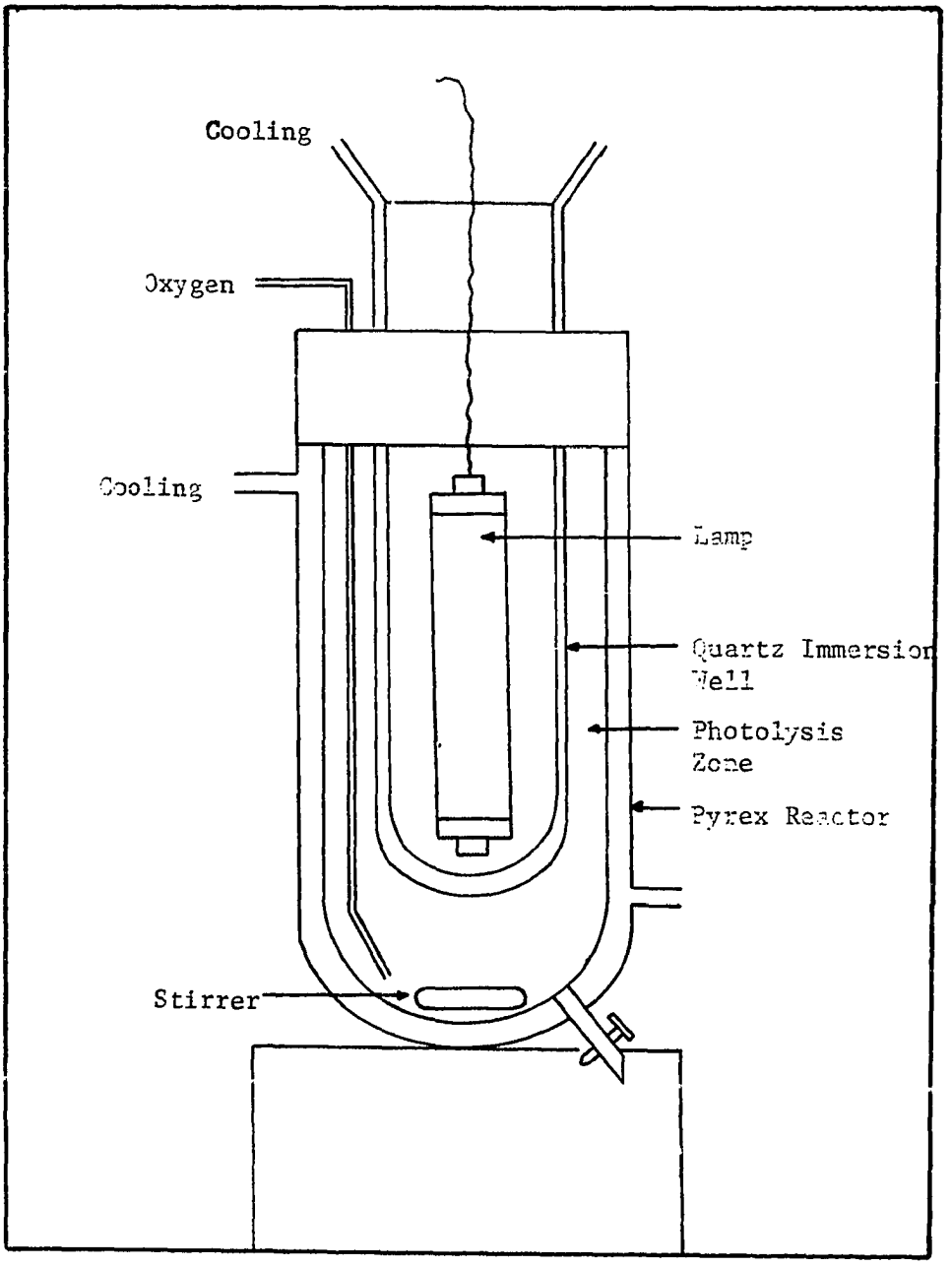


Figure C-1. Photochemical Reactor Diagram

APPENDIX D

COMPILATION OF DATA FROM PRELIMINARY EXPERIMENTS

TABLE D-1

IRRADIATION OF PHENOL SOLUTION USING 550 WATT HIGH-PRESSURE LAMP AT 150 MIN. REACTION TIME

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*			
			I	II	III	IV
504	-	-	-	-	0	-
504	-	-	-	65	-	-
500	-	-	43.5	-	-	-
500	-	-	-	-	-	60
500	Methylene Blue	100	-	-	0	-
500	Methylene Blue	500	-	-	0	-
500	Rose Bengal	52	-	-	0	-
500	Rose Bengal	100	-	-	0	-
500	Rose Bengal	500	-	-	0	-
500	ZnO	500	-	-	82.5	-
500	ZnO	1000	-	-	43.5	-
100	ZnO	87	-	-	80	-
100	ZnO	129	-	-	100	-
100	ZnO	175	-	-	100	-

TABLE D-1
(Continued)

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*			
			I	II	III	IV
500	ZnO	870	-	-	71	-
500	Acridine Orange	100	-	-	29	-
500	Acridine Orange	250	-	-	25	-
500	Acridine Orange	500	-	-	0	-
500	Acridine Orange	50	-	-	15	-
500	Rhodamine B	100	-	-	12	-
500	Rhodamine B	500	-	-	0	-
500	Eosin Yellow	100	-	-	46	-
500	Eosin Yellow	500	-	-	42	-

* I: without oxygen, quartz immersion well.
II: with oxygen; quartz immersion well.
III: with oxygen, borosilicate immersion well.
IV: with air; quartz immersion well.

TABLE D-2

IRRADIATION OF t-AMYL ALCOHOL USING 550 WATT HIGH-PRESSURE LAMP
AT 150 MIN. REACTION TIME

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*		
			I	II	III
1000	-	-	-	-	0
1000	-	-	-	60	-
1000	ZnO	200	-	-	38
1000	ZnO	920	-	-	50
1000	ZnO	1380	-	-	33
1000	ZnO	1840	-	-	30
1000	Eosin Yellow	105	-	-	0
1000	Eosin Yellow	500	-	-	0
1000	Acridine Orange	100	-	-	0
1000	Acridine Orange	500	-	-	0
1000	Rhodamine B	100	-	-	0

TABLE D-2
(Continued)

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*		
			I	II	III
1000	Rhodamine B	500	-	-	0
1000	Crystal Violet	100	-	-	0
1000	Crystal Violet	500	-	-	0
1000	Methylene Blue	100	-	-	0
1000	Methylene Blue	500	-	-	0
1000	Rose Bengal	100	-	-	0
1000	Rose Bengal	500	-	-	0

*same as in Table D-1.

TABLE D-3

IRRADIATION OF HEXYL-ACHOHOL USING 550 WATT HIGH-PRESSURE LAMP
AT 150 MIN. REACTION TIME

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*		
			I	II	III
500	-	-	0	-	-
500	-	-	-	29	-
500	ZnO	500	-	-	50
500	Eosin Yellow	100	-	-	15
500	Rose Bengal	100	-	-	0
500	Acridine Orange	100	-	-	0
500	Methylene Blue	100	-	-	0

*same as in Table D-1.

TABLE D-4

IRRADIATION OF HEXYL-AMINE SOLUTION USING 550 WATT HIGH-PRESSURE LAMP AT 150 MIN. REACTION TIME

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted Reaction Condition*		
			I	II	III
1000	-	-	0	-	-
1000	-	-	-	60	-
1000	ZnO	1000	-	-	0
1000	ZnO	250	-	-	0
1000	Eosin Yellow	500	-	-	34
1000	Acridine Orange	500	-	-	32
1000	Rose Bengal	500	-	-	45
1000	Methylene Blue	500	-	-	0

*same as in Table D-1.

TABLE D-5

PHOTODEGRADATION AND DIRECT PHOTOOXIDATION OF AN EMULSION OF XYLENE USING 550 WATT HIGH-PRESSURE LAMP AT 150 MIN. REACTION TIME

Concentration mg/l	% Reacted Reaction Condition*		
	I	II	III
875	64	-	-
875	-	100**	-
875	-	-	100**

* I: Photodegradation
II: Direct Photooxidation with oxygen
III: Direct Photooxidation with air

** the complete disappearance of xylene was partially due to stripping.

TABLE D-6

IRRADIATION OF AN EMULSION OF BENZENE USING 550 WATT HIGH-PRESSURE LAMP AT 150 MIN. REACTION TIME

Concentration mg/l	Sensitizer	Sensitizer Concentration mg/l	% Reacted** Reaction Condition*		
			I	II	III
450	-	-	82	-	-
450	-	-	-	91	-
450	ZnO	500	-	-	72
450	Eosin Yellow	100	-	-	0
450	Acridine Orange	100	-	-	0
450	Rose Bengal	100	-	-	0
450	Methylene Blue	100	-	-	0

*same as in Table D-1.

**corrected for reduction by stripping.

TABLE D-7

RATE OF PHOTOSENSITIZED OXIDATION OF PHENOL AS FUNCTION OF SENSITIZED/SUBSTRATE RATIO

Reaction Time Hours	% Reacted Reaction Condition*			
	I	II	III	IV
1	11.1	35.8	25	13.4
2	11.1	43.5	37.4	46.6
3	22	48.3	29.3	53.2
4	52.3	52.2	58.5	61.8

* I: 1000mg/1; ZnO/Phenol = 1:2
II: 1000mg/1; ZnO/Phenol = 1:1
III: 1000mg/1; ZnO/Phenol = 2:1
IV: 500mg/1; ZnO/Phenol = 1:2

TABLE D-8

RATE OF ZnO PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF PHENOL USING 550 HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*					
	I	II	III	IV	V	VI
1	36	53.6	24	20.8	25	8.9
2	48	57.3	30.5	25.6	29.4	28
3	69	62.5	43.6	41.8	37.5	31
4	72	75	52.3	50.8	41.6	35.6

*

I: 500 mg/l; Phenol/ZnO = 1:1
II: 500 mg/l; Phenol/ZnO = 1:2
III: 1000 mg/l; Phenol/ZnO = 1:1
IV: 1000 mg/l; Phenol/ZnO = 1:2
V: 1500 mg/l; Phenol/ZnO = 1:1
VI: 1500 mg/l; Phenol/ZnO = 1:2

TABLE D-9

RATE OF PHOTODEGRADATION AND DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF PHENOL USING 550 HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*					
	I	II	III	IV	V	VI
1	28.5	100	0	68.7	25	40
2	42.8	100	0	100	25	55
3	57.3	100	26.8	100	41.6	80
4	71.4	100	26.8	100	45.9	100

* I: 250mg/1; Photodegradation
II: 250mg/1; Direct Photooxidation
III: 500mg/1; Photodegradation
IV: 500mg/1; Direct Photooxidation
V: 750mg/1; Photodegradation
VI: 750mg/1; Direct Photooxidation

TABLE D-10

RATE OF DYE-PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF PHENOL USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*			
	I	II	III	IV
1	30.7	20	25.5	28.4
2	38.5	26.7	32.4	26.2
3	38.5	35.7	34.3	32.1
4	46.2	40	36.4	37.8

* I: 500mg/1; Eosin Yellow = 100mg/1
II: 500mg/1; Eosin Yellow = 500mg/1
III: 1000mg/1; Eosin Yellow = 100mg/1
IV: 1000mg/1; Eosin Yellow = 500mg/1

TABLE D-11

PIGMENT-PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF PHENOL (1000 mg/l and Sensitizer/Phenol = 1:1 Mole Ratio) USING HIGH-PRESSURE IMMERSION LAMP

Reaction Time, Hrs.	Sensitizer							
	ZnO(Used)		$ZnCO_3$		ZnS		TiO_2	
	% Reacted	% COD Removed	% Reacted	% COD Removed	% Reacted	% COD Removed	% Reacted	% COD Removed
1	28.7	0	9.1	0	0	0	0	0
2	38.2	3.7	13.7	0	0	0	0	0
3	57.3	12.1	18.2	0	0	0	21.1	5.5
4	57.3	12.7	17.2	3.8	0	0	31.6	9.1

TABLE D-12

RATE OF PHOTODEGRADATION AND PHOTOOXIDATION OF CYCLOHEXANONE IN AQUEOUS SOLUTION USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*					
	I	II	III	IV	V	VI
1	83.5	100	89	82	96	89
2	90	100	92	94	99	94
3	90	100	92	94	99	96
4	90	100	92	100	100	96

*
I: 475mg/1; Photodegradation
II: 475mg/1; Direct Photooxidation
III: 950mg/1; Photodegradation
IV: 950mg/1; Direct Photooxidation
V: 1900mg/1; Photodegradation
VI: 1900mg/1; Direct Photooxidation

TABLE D-13

RATE OF PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF CYCLOHEXANONE USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*					
	I	II	III	IV	V	VI
1	13.6	27.2	12	29.2	11.3	10.6
2	27.2	43.2	20.8	41.8	11.3	11.8
3	43.2	65.8	27.5	53.2	11.4	22.4
4	47.8	72.5	36.8	58.2	22.5	29.4

*
I: 500mg/1; Ketone/ZnO = 1:1
II: 500mg/1; Ketone/ZnO = 1:2
III: 1000mg/1; Ketone/ZnO = 1:1
IV: 1000mg/1; Ketone/ZnO = 1:2
V: 2000mg/1; Ketone/ZnO = 1:1
VI: 2000mg/1; Ketone/ZnO = 1:2

TABLE D-14

RATE OF PHOTODEGRADATION AND PHOTOOXIDATION OF ETHANOL
BY 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*					
	I	II	III	IV	V	VI
1	4.8	18.1	0	14.2	0	6.7
2	14.8	35.3	6	56	0	4.5
3	16	69.6	10	83	0	88.5
4	17.5	96	10	95	0	85.3

*
I: 395mg/1; Photodegradation
II: 395mg/1; Direct Photooxidation
III: 790mg/1; Photodegrdation
IV: 790mg/1; Direct Photooxidation
V: 1580mg/1; Photodegradation
VI: 1580mg/1; Direct Photooxidation

TABLE D-15

RATE OF ZnO SENSITIZED OXIDATION OF AQUEOUS SOLUTION OF EHTANOL
USING 550 HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition					
	I	II	III	IV	V	VI
1	30.5	14.3	28.3	26.2	18.4	18
2	43.5	23.8	38.5	43.2	21.2	30.7
3	48.5	31.3	50	52.2	26.4	36
4	51.5	33.3	61.8	59	35.8	38.5

*
I: 395mg/l; Ethanol/ZnO = 1:1
II: 395mg/l; Ethanol/ZnO = 1:2
III: 790mg/l; Ethanol/ZnO = 1:1
IV: 790mg/l; Ethanol/ZnO = 1:2
V: 1185mg/l; Ethanol/ZnO = 1:1
VI: 1185mg/l; Ethanol/ZnO = 1:2

Note: two peaks appeared on the chromatogram (at the same column temperature).

TABLE D-16

RATE OF PHOTODEGRADATION AND PHOTOOXIDATION OF AQUEOUS SOLUTION OF HEXYL ALCOHOL USING 550 HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*			
	I	II	III	IV
1	26.7	37.5	0	41.8
2	33.3	75	0	66.7
3	33.3	93	0	79
4	36.5	100	0	79

* I: 410mg/1; Photodegradation
II: 410mg/1; Direct Photooxidation
III: 820mg/1; Photodegradation
IV: 820mg/1; Direct Photooxidation

TABLE D-17

RATE OF ZnO SENSITIZED OXIDATION OF AQUEOUS SOLUTION OF HEXYL ALCOHOL USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*			
	I	II	III	IV
1	25.5	4.85	18.2	36.8
2	48	8.7	31	50
3	66.6	17.4	47.7	60
4	76.5	18.05	51.8	66.1

* I: 410mg/1; Hexyl Alcohol/ZnO = 1:1
II: 410mg/1; Hexyl Alcohol/ZnO = 1:2
III: 820mg/1; Hexyl Alcohol/ZnO = 1:1
IV: 820mg/1; Hexyl Alcohol/ZnO = 1:2

TABLE D-18

RATE OF PHOTODEGRADATION AND PHOTOOXIDATION OF AQUEOUS SOLUTION OF HEXYL-AMINE USING 550 HIGH-PRESSURE LAMP

Reaction Time Hours	% Reacted Reaction Condition*			
	I**	II+	III+	IV
1	0	0	0	15.3
2	0	0	0	23
3	0	0	0	23
4	0	0	0	23

* I: 382mg/1; Photodegradation
II: 382mg/1; Direct Photooxidation
III: 763mg/1; Photodegradation
IV: 763mg/1; Direct Photooxidation

** the solution became turbid after 1 hour.

+ two peaks appeared on the chromatogram.

APPENDIX E

COMPILATION OF DATA FROM SUBSEQUENT EXPERIMENTS

TABLE E-1

EFFECT OF PHOTOCHEMICAL REACTION OF THE BOD/COD RATIO OF VARIOUS ORGANIC COMPOUNDS UNDER DIFFERENT REACTION CONDITIONS USING 550 WATT HIGH-PRESSURE LAMP

Compound	Concentration mg/1	Process*	BOD/COD		pH	
			t = 0	t = 4 hrs.	t = o	t = 4 hrs.
Ethanol	1578	a	1	.93	6.6	3.1
Cyclohexanone	947	a	.65	.57	7.1	3.5
Cyclohexanone	947	b	.6	.5	7.2	3.8
Ethanol	395	c	.9	.8	9.5	7.4
Ethanol	395	c	1	.94	9.8	8.7
Ethanol	789	c	.98	1	10.7	7.1
Ethanol	789	c	.87	.8	10.2	6.5
Ethanol	1189	c	.85	.77	9.4	6.3
Cyclohexanone	474	c	.5	.55	7.9	6.8
Cyclohexanone	947	c	.6	.66	7.3	6.7
Cyclohexanone	947	c	.55	.61	7.8	6.2
Cyclohexanone	1894	c	.55	.54	7.1	6.3
Cyclohexanone	1894	c	.45	.51	7.2	6
Hexanol	410	c	.8	.7	8	5.8
Hexanol	410	c	.75	.82	7.8	6.4
Hexanol	820	c	.75	.68	7.5	6.3
Hexanol	820	c	.74	.7	7.4	6.5

TABLE E-1
(Continued)

Compound	Concentration mg/l	Process*	BOD/COD		pH	
			t = 0	t = 4 hrs.	t = 0	t = 4 hrs.
Ethanol	395	d	1	1	6.9	6.5
Ethanol	789	d	.67	.65	6.7	6.5
Ethanol	789	d	.39	.43	6.9	6.6
Ethanol	1578	d	.8	.7	7.1	4.3
Ethanol	1578	d	.49	.54	6.6	5
Cyclohexanone	474	d	.77	.85	7.2	5.5
Cyclohexanone	474	d	.15	.19	7.2	4.5
Cyclohexanone	1894	d	.05	.08	7.1	4.5
Cyclohexanone	1894	d	.06	.04	6.3	6.1
Cyclohexanone	1894	e	.24	.3	10.2	3.4
Hexanol	1640	e	.65	.59	7.2	3.5
Phenol	500	c	.9	1	6.8	6.5
Phenol	1000	c	.8	.9	7.5	6.2
Phenol	1000	c	.9	1	7.3	6.2
Phenol	1500	c	1	1	7.3	6
Phenol	1500	c	.97	.9	7.4	6.5
Phenol	500	f	1	1	8.6	4

TABLE E-1
(Continued)

Compound	Concentration mg/l	Process*	BOD/COD		pH	
			t = o	t = 4 hrs.	t = o	t = 4 hrs.
Phenol	500	f	1	1	6.8	4.6
Phenol	1000	f	1	1	7	3.5
Ethanol	395	a	1	.62	6.3	3.5
Ethanol	790	a	1	.49	6.2	3.2
Cyclohexanone	474	b	.6	.32	6.9	3.9
Hexyl-amine	763	b	.57	.27	10.9	8.4
Hexanol	410	a	.81	.37	7.7	2.8
Hexanol	820	a	.95	.54	7	2.9
Phenol	250	a	1	.4	7.3	6.9
Phenol	250	b	1	.74	7.1	3.5
Phenol	500	a	.91	.27	7.3	2.2
Phenol	500	b	.97	.7	6.8	3.2
Phenol	750	a	1	.49	6.7	2.1
Ethanol	1184	c	.81	.65	9.4	6.3
Cyclohexanone	474	c	.6	.38	8.3	6.3
Hexyl-amine	382	c	.56	.32	10.9	6.9

TABLE E-1
(Continued)

Compound	Concentration mg/l	Process*	BOD/COD		pH	
			t = 0	t = 4 hrs.	t = 0	t = 4 hrs.
Hexyl-amine	763	c	.72	.35	11.2	8.8
Hexyl-amine	763	c	.45	.25	11.4	10
Ethanol	395	d	.71	.49	5.7	5
Cyclohexanone	1894	e	.35	.12	7.5	3.8
Phenol	1000	f	.7	.45	7.3	5
Cyclohexanone	474	a	.21	.49	6.8	3.8
Cyclohexanone	1894	a	.22	.55	7.1	3.3
Cyclohexanone	1894	b	.27	.43	7.1	3.4
Phenol	750	b	.8	1	6.6	3.2
Hexanol	420	c	.73	1	11	6.8
Phenol	500	c	.55	.75	7.2	6

*a: Direct Photooxidation
b: Photodegradation
c: ZnO Sensitized Oxidation
d: Acridine Orange Sensitized Oxidation
e: Rose Bengal Sensitized Oxidation
f: Eosin Yellow Sensitized Oxidation

TABLE E-2

EXTENT OF PHOTODEGRADATION OF AQUEOUS SOLUTION OF PHENOL (500 mg/1)
USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	808	940	.86	-	0
1	6.7	930	940	.98	-	0
2	13.4	747	940	.79	7.5	0
3	20.1	567	940	.6	29.8	0
4	33.3	686	940	.73	15.1	0
5	33.3	381	940	.4	52.8	0
6	33.3	564	940	.6	30.2	0
7	33.3	564	940	.6	30.2	0
8	33.3	503	940	.54	37.7	0

TABLE E-3

EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF PHENOL (500mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	0	930	916	1	-	-
1	68.6	442	833	.53	52.5	9.1
2	89.7	198	667	.3	78.7	27.2
3	95	198	417	.48	78.7	54.5
4	100	442	392	1.32	52.5	63.4
5	100	137	333	.35	85.3	57.3
6	100	137	156	.88	85.3	82.9
7	100	137	156	.88	85.3	82.9
8	100	16	78	.19	98.4	91.5

TABLE E-4

EXTENT OF PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF PHENOL (500 mg/1, Phenol/ZnO = 1:2, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	0	778	941	.83	-	-
1	43.5	625	784	.8	19.8	16.7
2	52.2	564	627	.9	27.5	33.4
3	65.6	442	627	.71	43.2	33.4
4	78.4	381	705	.54	51	25.2
5	82.5	370	627	.59	52.4	33.4
6	87.5	198	392	.51	74.5	58.3
7	91.5	137	235	.59	82.3	75
8	95.5	76	78	.97	90.2	91.7

TABLE E-5

THE EFFECT OF pH ON THE EXTENT OF THE DIRECT OXIDATION OF AQUEOUS SOLUTION OF PHENOL (1000 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/l		
	pH = 2	pH = 7	pH = 12
0	2318	2255	2271
1	2139	2183	2156
2	1959	2083	2091
3	1812	1934	1926
4		1766	1893
4 1/2	1649		
5		1649	1761
6	1518	1583	1679
7	1241	1466	1597
7 3/4			1547
8	1028	1399	
9 1/2			1415

TABLE E-6

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF PHENOL AT DIFFERENT INITIAL CONCENTRATIONS USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining				
	100 mg/1	250 mg/1	350 mg/1	500 mg/1	1000 mg/1
0	237	563	810	1157	2255
½	195	498	737		
1	171	457	678	1020	2183
1½	49	416	640		
2	24	367	575	883	2083
3	16	171	502	761	1934
4	16	25		656	1766
4¼			340		
5	16	16	138	476	1649
6	0	16	16	137	1583
7	0	8	0	0	1466
8	0	0	0	0	1399

TABLE E-7

EXTENT OF PHOTODEGRADATION OF CYCLOHEXANONE IN AQUEOUS SOLUTION (947 mg/l)
USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/l	COD Remaining mg/l	BOD/COD	% Removal	
					BOD	COD
0	-	1205	2049	.59	-	-
1	100	1388	2049	.68	-	0
2	100	961	1967	.49	20.2	4
3	100	961	1967	.49	20.2	4
4	100	961	1967	.49	20.2	4
5	100	961	1885	.51	20.2	8
6	100	961	1721	.56	20.2	16
7	100	716	1721	.42	40.6	16
8	100	961	1639	.59	20.2	20

TABLE E-8

EXTENT OF ZnO SENSITIZED OXIDATION OF AQUEOUS SOLUTION OF CYCLOHEXANONE (947 mg/1, Ketone/ZnO = 1:2, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1204	2066	.58	-	-
1	17.6	1204	2066	.58	0	0
2	33.3	778	1818	.43	35.4	12
3	45.7	598	1662	.35	50.3	19
4	52.5	716	1735	.41	40.5	16
5	59.8	655	1570	.42	45.6	24
6	65	533	1404	.38	55.7	32
7	70.6	656	1487	.44	45.5	28
8	75.5	594	1404	.42	50.7	32

TABLE E-9

EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF CYCLOHEXANONE (947 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1571	1983	.79	-	-
1	100	961	1652	.58	38.8	16.7
2	100	808	1240	.65	48.6	37.5
3	100	625	1157	.54	60.2	41.7
4	100	442	1074	.41	71.9	45.8
5	100	441	992	.45	71.9	50
6	100	381	744	.51	75.7	62.5
7	100	381	661	.58	75.7	66.7
8	100	403	413	.97	74.3	79.2

TABLE E-10

THE EFFECT OF pH ON THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF CYCLOHEXANONE (1000 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/1		
	pH = 2	pH = 7	pH = 12
0	2128	2283	2259
1	1712	1817	2092
2	1472	1550	1925
3	1328	1383	1757
4	1120	1200	1572
5	960	1117	1423
6	784	967	1238
7	576	783	1071
7 3/4			954
8	400	633	

TABLE E-11

EXTENT OF ZnO SENSITIZED OXIDATION OF AQUEOUS SOLUTION OF HEXYL ALCOHOL (820 mg/1, Alcohol/ZnO = 1:2, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1296	1983	.65	-	-
1	20.8	1235	1653	.75	4.7	16.6
2	41.6	1174	1404	.84	9.4	29.2
3	43.8	1113	1404	.79	14.1	29.2
4	62.7	1052	1983	.53	18.8	0
5	64.5	991	1818	.55	23.5	8.3
6	70.7	869	1239	.71	32.9	37.5
7	77	930	1156	.84	28.2	41.7
8	79.3	869	1156	.75	32.9	41.7

TABLE E-12

EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF HEXYL ALCOHOL (820 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1327	1983	.67	-	-
1	31.1	1479	1818	.81	-	8.3
2	60.4	1052	1487	.71	20.7	25
3	77.8	808	1404	.58	39.1	29.2
4	90	503	1239	.41	62.1	37.5
5	94.8	442	1074	.41	66.7	45.8
6	96.5	442	774	.59	66.7	62.5
7	100	442	774	.59	66.7	62.5
8	100	320	496	.65	75.9	75

TABLE E-13

THE EFFECT OF pH ON THE EXTENT OF DIRECT PHOTOEXODATION OF AQUEOUS SOLUTION OF HEXYL ALCOHOL (1000 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/1		
	pH = 2	pH = 7	pH = 12
0	1943	1983	1790
1	1780	1833	1645
2	1584	1617	1516
3	1437	1467	1435
4		1267	1339
4½	1208		1226
5		1117	
6	996	1017	1145
7	800		1000
7¼		867	
8	686	750	903

TABLE E-14

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTIONS OF HEXYL ALCOHOL AT DIFFERENT INITIAL CONCENTRATIONS USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/1			
	0.1 ml/1	0.25 ml/1	0.50 ml/1	1 ml/1
0	201	473	935	1983
½	178	451	930	
1	147	376	889	1833
1½	139	298	808	
2	93	210	695	1617
2½	62		585	
3	54	45	509	1467
4	15		284	1267
4½		8		
5	8		67	1167
6	0	0	30	1017
7	0	0	22	
7¼				867
8			15	750

TABLE E-15

EXTENT OF PHOTODEGRADATION OF AQUEOUS SOLUTION OF ETHANOL (790 mg/l)
USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/l	COD Remaining mg/l	BOD/COD	% Removal	
					BOD	COD
0	-	1174	1646	.71	-	-
1	6	1052	1254	.84	10.4	23.8
2	8	930	1254	.74	20.8	23.8
3	18	930	1176	.79	20.8	28.5
4	18	1052	1490	.71	10.4	9.5
5	24	1052	1333	.79	10.4	19
6	26	930	1008	.85	20.8	33.3
7	29	930	1098	.85	20.8	33.3
8	33	930	1098	.85	20.8	33.3

TABLE E-16

EXTENT OF PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF ETHANOL (790 mg/1, Ethanol/ZnO = 1:1, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1052	1481	.71	-	-
1	31.4	869	1481	.58	17.4	0
2	39.8	686	1234	.56	34.8	16.7
3	50	747	1349	.55	29	8.9
4	58.3	747	1297	.58	29	12.4
5	64.9	747	1234	.61	29	16.7
6	68.8	747	1070	.69	29	27.8
7	70.8	625	905	.69	40.6	38.9
8	75	686	905	.76	34.8	38.9

TABLE E-17

EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF ETHANOL (790 mg/1) USING 550 HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1083	1551	.7	-	-
1	25.5	961	1224	.79	11.3	21.1
2	53	716	1224	.59	33.9	21.1
3	90	350	735	.48	67.7	52.6
4	100	168	245	.69	84.5	84.5
5	100	64	83	.78	94.1	94.7
6	100	325	82	-	70	94.7
7	100	45	0	-	95.8	100
8	100	106	0	-	90.2	100

TABLE E-18

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF PROPANOL (805 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	1143	1596	.72	-	-
1	34.2	1083	1386	.78	5.2	13.2
2	64	778	1176	.66	31.9	26.3
3	78.7	595	966	.62	47.9	39.5
4	95.6	357	674	.53	68.8	58
5	100	107	126	.85	90.6	92.1
6	100	45	42	1.07	96.1	97.4
7	100	0	42	0	100	97.4
8	100	0	0	-	100	100

TABLE E-19

EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF t-AMYL ALCOHOL (780 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	% Reacted	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
					BOD	COD
0	-	483	2116	.21	-	-
1	44.8	248	1618	.15	41.3	23.5
2	78.9	245	1368	.18	42.1	35.3
3	85.4	364	1245	.29	13.9	41.2
4	91.5	425	1120	.38	0	47.1
5	94.8	364	632	.59	13.9	70.6
6	97.8	308	456	.68	27.2	78.4
7	100	484	378	-	-	82.1
8	100	250	207	-	40.9	90.2

TABLE E-20

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTIONS OF LOW MOLECULAR WEIGHT ALCOHOLS AND ORGANIC ACIDS USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/l			
	Methanol	Formic Acid	Ethanol	Acetic Acid
0	1085	1048	1551	745
½	1101	863		656
1	1085	661	1224	559
1½	1020	468		452
2	939	293	1224	362
3	696	65	735	161
4	453		245	40
4¼		40		
5	243	40	82	
6	40	24	82	8
7	16	0	0	0
7½	16	0	0	0
8	0	0	0	0

TABLE E-21

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTIONS OF LOW MOLECULAR WEIGHT ALCOHOLS AND ORGANIC ACIDS USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	COD Remaining, mg/l			
	Propanol	Propionic Acid	Butanol	Iso-butanol
0	1596	1358	1853	1854
1/2			1837	1658
2/3		864		
1	1386	724	1707	1496
1 1/2		576	1522	1349
2	1176	461	1431	1211
3	966	214	1138	935
4	672			707
4 1/4		107	886	
5	126	91	732	488
6	42	74	512	252
7	42	58	268	106
8	0	33	130	16

TABLE E-22

THE EXTENT OF ZnO PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF DODECYL SODIUMSULFATE (750 mg/1, Dodecyl Na-Sulfate/ZnO = 1:2, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	1025	1255	.82	-	-
1	968	1171	.83	5.6	6.7
2	766	1129	.68	25.3	11.2
3	885	1129	.78	13.7	11.2
4	885	1046	.85	13.7	16.7
5	765	962	.8	25.4	23.3
6	765	967	.8	25.4	23.3
7	646	962	.67	36.9	23.3
8	766	878	.88	25.3	30

TABLE E-23

THE EXTENT OF DIRECT OXIDATION OF DODECYL SODIUMSULFATE IN AQUEOUS SOLUTION (750 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	1126	1380	.82	-	-
1	833	1255	.66	26	9.1
2	479	1046	.46	57.6	24.2
3	542	1004	.54	51.9	27.2
4	365	837	.44	67.6	39.3
5	306	711	.43	72.8	48.5
6	367	502	.73	67.4	63.6
7	248	335	.74	77.9	75.7
8	303	209	1.58	73.1	84.8

TABLE E-24

THE EXTENT OF ZnO PHOTOSENSITIZED OXIDATION OF AQUEOUS SOLUTION OF SODIUM-STEARATE (1000 mg/1, Na-Stearate/ZnO = 1:2, Mole Ratio) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	1318	2773	.48	-	-
1	1142	1828	.63	13.4	34.1
2	1727	1260	-	-	54.6
3	732	1932	.35	44.5	30.3
4	849	1932	.44	35.6	30.3
5	790	924	.86	40.1	66.7
6	849	1807	.47	35.6	34.8
7	866	2017	.43	34.2	27.6
8	1254	1386	.9	4.8	50

TABLE E-25

THE EXTENT OF DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF SODIUM STEARATE USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/l	COD Remaining mg/l	BOD/COD	% Removal	
				BOD	COD
0	542	2689	.2	-	-
1	505	1933	.26	6.8	28.1
2	542	1218	.45	0	54.7
3	483	1134	.4	11.1	57.8
4	425	1092	.4	21.6	59.4
5	425	883	.48	21.6	67.2
6	73	882	.09	86.5	67.2
7	659	882	.75	-	67.2
8	307	672	.46	43.4	75

APPENDIX F

COMPILATION OF DATA FROM FINAL EXPERIMENTS

TABLE F-1

THE EXTENT OF DIRECT PHOTOOXIDATION OF EMULSION OF VEGETABLE OIL (Soybean Oil, 5 ml/l) USING 550 HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/l	COD Remaining mg/l	BOD/COD	% Removal	
				BOD	COD
0	1932	7468	.26	-	-
1	2108	9054	.23	-	-
2	527	9128	.06	72.7	-
3	819	8381	.1	57.6	-
4	0	8962	0	100	-
5	176	4149	.04	90.8	44
6	0	5228	0	100	30
7	237	4149	.06	87.7	44
8	176	2821	.06	90.8	62.1

TABLE F-2

THE EXTENT OF DIRECT PHOTOOXIDATION OF EMULSION OF VEGATABLE OIL
(Soybean Oil, 2.5 ml/1) USING 550 HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	1346	2314	.58	-	-
1	762	2892	.26	43.4	-
2	538	3554	.15	60.8	-
3	878	4132	.21	34.8	-
4	761	3140	.24	43.5	-
5	410	1983	.21	69.5	14.3
6	410	1735	.24	69.5	25
7	527	1901	.28	60.8	17.8
8	644	1487	.43	52.3	35.7

TABLE F-3

THE EXTENT OF DIRECT PHOTOOXIDATION OF AN EMULSION OF LINOLEIC ACID (2.5 ml Acid/1000 ml Water) USING 550 HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/l	COD Remaining mg/l	BOD/COD	% Removal	
				BOD	COD
0	884	2778	.31	-	-
1	1189	2387	.49	-	14.3
2	762	1746	.43	13	37.1
3	762	2381	.32	13	14.3
4	732	1984	.36	13	28.6
5	701	2614	.26	20	5.9
6	1128	2382	.47	-	14.3
7	640	2222	.28	27.6	20
8	640	2222	.28	27.6	20

TABLE F-4

THE EXTENT OF DIRECT PHOTOOXIDATION OF SUSPENSION OF PAPER PULP (Approx. 150 mg/1) USING 550 WATT HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	146	996	.15	-	-
1	204	954	.21	-	4.1
2	146	1120	.13	-	-
3	263	996	.26	-	-
4	146	1162	.13	-	-
5	263	871	.3	-	12.5
6	205	871	.24	-	-
7	263	871	.3	-	-
8	263	954	.28	-	4.1

TABLE F-5

THE EXTENT OF PHOTOSENSITIZED OXIDATION OF SUSPENSION OF PAPER PULP
(Approx. 150 mg/1, ZnO = 500 mg/1) USING 550 HIGH-PRESSURE LAMP

Reaction Time, Hrs.	BOD Remaining mg/1	COD Remaining mg/1	BOD/COD	% Removal	
				BOD	COD
0	615	1452	.42	-	-
1	205	742	.28	66.7	48.9
2½	88	664	.13	84.1	54.3
3½	205	539	.38	66.7	62.9
4½	88	580	.15	84.1	60
6½	88	664	.13	84.1	54.3
8	205	415	.48	66.7	71.4

TABLE F-6

DIRECT PHOTOOXIDATION OF FREE CYANIDE USING 550 WATT HIGH-PRESSURE LAMP AT pH:12

Reaction Time, Hrs.	CN^- Remaining, mg/l	% Removal
0	118	-
1	19.7	83.3
2	4.9	95.8
3	0	100

TABLE F-7

DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE
USING 550 WATT HIGH-PRESSURE LAMP AT pH:12

Reaction Time, Hrs.	CN^- Remaining mg/l	% Removal
0	2283	-
1	2027	11.2
2	1870	18.1
3	1712	25
4	1476	35.3
5	1279	44
6	958	58
7	886	61.2
8	708	69

TABLE F-8

DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE
USING 550 WATT HIGH-PRESSURE LAMP AT pH:12

Reaction Time, Hrs.	CN^- Remaining, mg/1	% Removal
0	14250	-
1	13950	2.1
2	13650	4.2
4	13150	7.7
5	12950	9.1
7	12650	11.2
7½	12550	11.9

TABLE F-9

DIRECT PHOTOOXIDATION OF AQUEOUS SOLUTION OF FREE CYANIDE
USING 550 WATT HIGH-PRESSURE LAMP AT pH:12

Reaction Time, Hrs.	CN^- Remaining, mg/1	% Removal
0	118,080	-
1	98,400	16.7
2	98,400	16.7
3	98,400	16.7
4	98,400	16.7
5	96,432	18.3
6	94,464	20
10	90,528	23.3